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VOLUME 36 MAY 1958 NUMBER 5

THE MOLECULAR WEIGHT OF POLYETHYLENE AND OF OTHER HIGH-MOLECULAR-WEIGHT ORGANIC COMPOUNDS[1]

R. TREMBLAY,[2] A. F. SIRIANNI, AND I. E. PUDDINGTON

ABSTRACT

The temperature range of the measurement of vapor-pressure depression using a sensitive differential mercury micromanometer has been extended, and the behavior of a series of polyethylene samples having a molecular-weight range of 2500 to 24,000 was examined in toluene solutions at 75° C. Good agreement was obtained between vapor-pressure lowering and other means of determining number-average molecular weights of several special compounds.

INTRODUCTION

Number-average molecular weights lower than about 40,000 have been determined satisfactorily for a number of compounds of known constitution and for a series of vinyl-acetate polymers, by measuring the differences in vapor pressure between solutions of these substances and the pure solvent (1, 2, 3). The present communication describes similar measurements on a series of polymers of ethylene prepared by a high-pressure process and obtained through the courtesy of Canadian Industries Limited. The individual samples designated as melt index 200,000, 20,000, 7000, 700, 2, and 0.2 cover an approximate molecular-weight range of 2500 to 24,000.

It has been shown that individual samples of polyethylene can have weight-average–number-average molecular weight ratios as high as 70 with very broad distributions of the molecular sizes (4, 5, 6, 7). Differences of 25% in number-average molecular weight, attributed to membrane permeability, have been found when the same samples were examined osmometrically and cryoscopically (8). Increases in $\bar{M}_n$ as large as 100% have been effected with no change in the melt index by mild extractive fractionation (8). It has also been suggested that the result obtained may be influenced by the solvent used in ebulliometric measurements (9). It therefore seemed worth while to test the usefulness of an additional method for measuring $\bar{M}_n$, which is not too restricted in temperature of operation and not subject to membrane permeability, in the characterization of these interesting polymers.

Since polyethylene has limited solubility in most solvents below about 70° C. (10, 11), it was necessary to raise the temperature at which the vapor-pressure measurements were made from 55° C., which was used for most of the previous work, to 75° C. A number of comparative determinations were made on polymers of ethylene oxide and an esterified

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[2]*National Research Council Postdoctorate Fellow 1954–56. Present address: Canadian Industries Limited, McMasterville, Quebec.*

sucrose* that had molecular weights in the vicinity of 3000 and 1800 respectively and which had been examined by other methods.

APPARATUS AND EXPERIMENTAL

The apparatus and experimental technique have already been described (1, 2). Molecular-weight determinations on carbowax and sucrose myristate were carried out both in benzene at 42.5° C. and in toluene at 75° C. All determinations on polyethylene were made in toluene at 75° C. Solutions in all cases were optically clear and no evidence of insolubility, which would lead to fictitiously high values, was noted.

The dried polymers were stored *in vacuo* and 0.7 to 4 mg. quantities were used in preparing the solution. A drop of redistilled solvent was used to stick the newly weighed samples to their containers to reduce the danger of mechanical loss during subsequent operations. Care was taken to avoid overheating the polymers, especially when in contact with air, to minimize the possibility of molecular degradation. Solutions of the polymer were prepared in the usual way by condensing a known amount of solvent on the solid polymer after the sample holder had been sealed to the apparatus and the assembly evacuated.

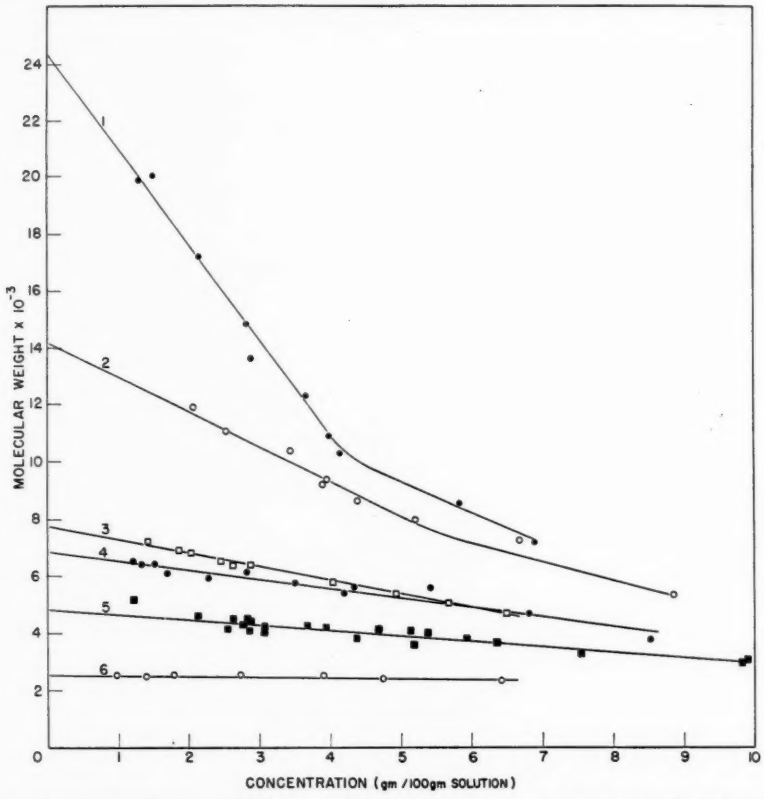

FIG. 1. Apparent molecular weight versus solute concentration for a series of polyethylene samples in toluene at 75° C. Curve 1, melt index 0.2; Curve 2, melt index 2; Curve 3, melt index 700; Curve 4, melt index 7000; Curve 5, melt index 20,000; Curve 6, melt index 200,000.

Kindly donated by Professor R. U. Lemieux, University of Ottawa, Ottawa.

RESULTS

The variation of apparent molecular weight with solution concentration for the series of polyethylenes is shown in Fig. 1. These values were calculated from Raoult's law. In estimating solution concentrations, corrections for the nonideality of the solvent vapor have been applied using Berthelot's equation of state and the critical data. However, without this correction, only a very small error is introduced in the molecular weight at infinite dilution. While it is evident that the apparent molecular weight of polyethylene samples having melt indexes of 0.2 and 2 is not a linear function of concentration over the whole range studied, a straight line fits the experimental points reasonably well at the lower concentrations. There is little evidence of curvature for all other samples and a straight line fits the experimental points over the whole concentration range covered. Similar behavior was observed for polyvinyl acetate in benzene at 55° C. (2).

The solute–solvent interaction coefficient, μ_1, of the system polyethylene–toluene was calculated from the well-known theoretical equation due to Huggins (12, 13) and Flory (14, 15)

$$\phi = (\ln a_1 - \ln V_1)/V_2 - 1 = \bar{V}_1/\bar{V}_2 + \mu_1 V_2,$$

where the symbols have their usual meaning.

The linear plots of ϕ vs. V_2 for the various polyethylene samples are shown in Fig. 2.

In calculating the solution concentration, it was assumed that the volumes of solute and solvent are additive (16) and the value for the density of ethylene polymer was taken as 0.92. The density of polyethylene in the molecular-weight range of 10,000 to 26,000 varies from 0.91 to 0.93 (17).

The molecular weights obtained from Raoult's law and those calculated from the

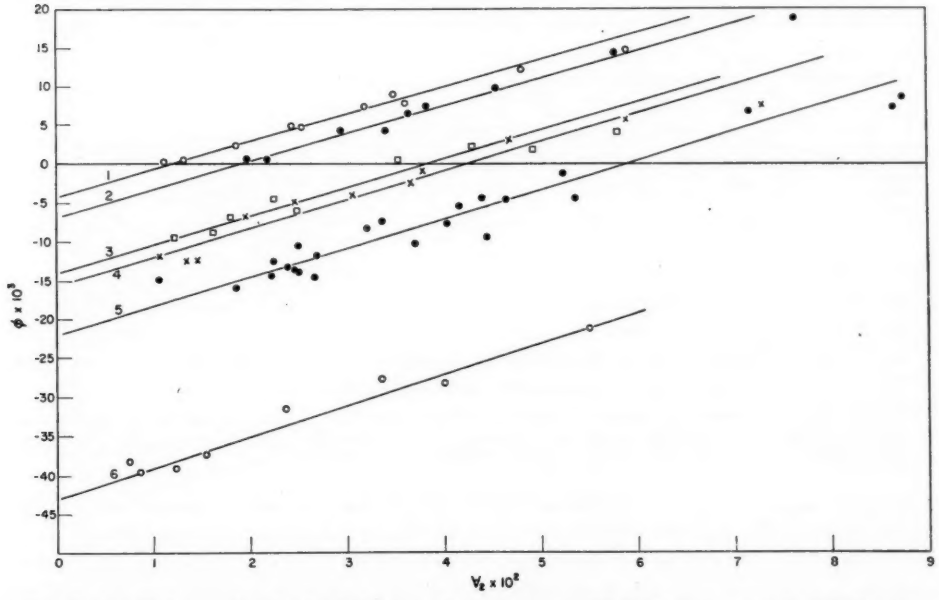

FIG. 2. ϕ vs. V_2 for a series of polyethylene samples in toluene at 75° C. Curve 1, melt index 0.2; Curve 2, melt index 2; Curve 3, melt index 700; Curve 4, melt index 7000; Curve 5, melt index 20,000; Curve 6, melt index 200,000.

Huggins–Flory equation, and values of μ_1, are shown in Table I. Also included are values obtained for the same samples in another laboratory with an ebulliometric procedure. While probably not strictly comparable some literature values of $\bar{M}_n$ are included for polyethylene of similar melt viscosity.

TABLE I

NUMBER-AVERAGE MOLECULAR WEIGHTS FOR A SERIES OF POLYETHYLENE POLYMERS

	Molecular weight				
Melt index	Raoult's law	Huggins–Flory	Ebulliometric	Literature values	μ_1
200,000	2550	2420	2500	1700[a]	0.40
20,000	4800	4720	4700	4000[a]	0.38
7,000	6850	6700	7100	5300[a]	0.37
700	7750	7410	6950	—	0.37
2	14150	14820	10400	32000[b] 25000[c] 17900[d]	0.36
0.2	24350	24420	18450		0.36

[a]*Harris (18), ebulliometric.*
[b]*Harris, osmometric.*
[c]*Smith (9), osmometric.*
[d]*Smith, ebulliometric.*

The results of the molecular-weight determinations for some other organic substances are shown in Fig. 3. Curves 1 and 2 were obtained for a sample of commercial carbowax.

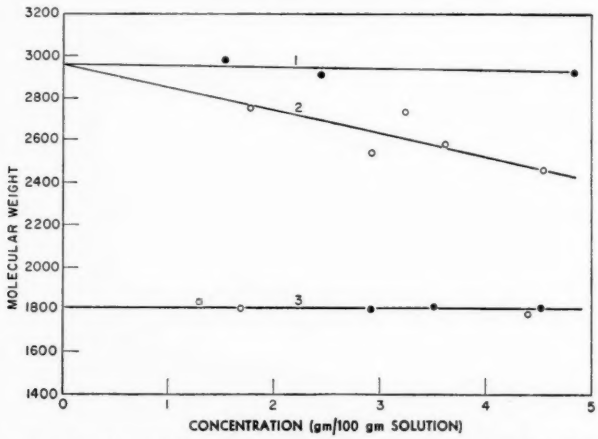

FIG. 3. Apparent molecular weight vs. solute concentration for a sample of carbowax and sucrose myristate. Curve 1, first measurements on carbowax; Curve 2, normal measurements; Curve 3, sucrose myristate (open circle, in toluene at 75° C.; closed circle, in benzene at 42.5° C.).

The first determinations were found to be independent of concentration; subsequent determinations were characterized by Curve 2. While the reason for this behavior is not too clear, the phenomenon has been observed previously with some samples of polyvinyl acetate and may be due to a slight amount of residual moisture trapped in the polymer and slightly reducing its solubility, causing the initial solutions to behave like an "ideal"

system. The molecular weight at infinite dilution was virtually identical for both curves, however. Curve 3 was obtained for a sample of sucrose myristate in benzene at 42.5° C. and in toluene at 75° C. A summary of the results for carbowax and sucrose myristate using the vapor-pressure lowering technique compared to other methods is given in Table II.

TABLE II

MOLECULAR WEIGHT OF CARBOWAX AND SUCROSE MYRISTATE OBTAINED BY DIFFERENTIAL MANOMETRY AND BY OTHER METHODS

Solute	Solvent	Mol. wt.	Method
Carbowax	Benzene	2960	Vapor pressure
Carbowax		2975	End-group analysis
Sucrose myristate	Benzene	1813	Vapor pressure
Sucrose myristate	Toluene	1813	Vapor pressure
Sucrose myristate	Benzene	1820	Cryoscopic

DISCUSSION

The similarity in the $\bar{M}_n$ values obtained when the results of cryoscopic and end-group analysis are compared to the vapor-pressure procedure lends support to the confidence that may be placed in that method. Unfortunately molecular weights of about 3000 are approaching the maximum values with which the available facilities for the former two methods are useful and it was not possible to extend the comparison.

Table I indicates satisfactory agreement between the two methods of treating the vapor-pressure data. The value of μ_1 found in this work is close to the value of 0.42 previously reported for polyethylene of melt index 200,000 in benzene at 80° C. (18). Values of 0.29 and 0.31 found for polyethylene samples having melt indexes of 20,000 and 7000 respectively in toluene at 110° C. (18) differ from the values obtained here in the expected direction when the temperature difference at which the measurements were made is considered. In contrast to the behavior of other polymers (2, 3, 13) there was virtually no dependence of the numerical value of μ_1 on molecular weight. This observation agrees with the findings of Muthana and Mark (17) and of Harris (18).

Differences between $\bar{M}_n$ values found here and those reported in the literature for polyethylene of similar melt index are not excessive in view of the variations noted recently in results obtained when the same sample of polymer is examined by different methods, and the large increase in $\bar{M}_n$ caused by the selective removal of about 1% of the sample (8).

No particular difficulty was found in the operation of the vapor-pressure apparatus at 75° C. Vapor-pressure differences normally become constant sufficiently quickly to allow check readings on the manometer at 60–90-minute intervals. It might be anticipated that volatility of mercury could become troublesome, however, if the operating temperature were raised too much higher. High-temperature operation might necessitate substitution of the mercury manometer with some form of diaphragm gauge and the cutoffs with valves. Under the present system of operation the limit on the precision of the measurement appeared to be controlled by variation in ΔP rather than by the ability of the manometer to measure these differences accurately.

The agreement between the results of the vapor-pressure and the ebulliometric procedures is excellent for the lower-molecular-weight polymers. Since several unrecorded measurements at 85° C. indicated the same molecular weight as shown for the sample of melt index 2 at 75° C., the discrepancy in the results of the two methods for the

higher-molecular-weight polymers does not appear to be due to incomplete solubility of the polymer at 75°. It may, however, be related to possible surface activity of these samples in the solvents used.

With the exception of the Huggins treatment shown in Fig. 2, the more conventional methods of presenting the experimental data offered little improvement in linearity of the curves obtained, over the plot of apparent molecular weight vs. concentration, and the simpler procedure was therefore used. It seems probable, however, that the molecular weights shown at infinite dilution may be slightly low because the linear extrapolation actually employed may not be entirely justified.

ACKNOWLEDGMENT

We are deeply indebted to Dr. W. R. Blackmore, Canadian Industries Limited, for the ebulliometric results included in Table I.

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REACTOR NEUTRON-CAPTURE CROSS SECTION OF 18-MINUTE Rb^{88} [1]

J. C. Roy, P. J. Berry,[2] and L. P. Roy

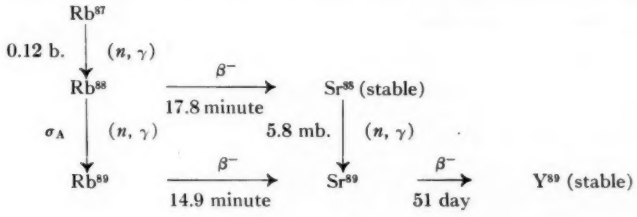
ABSTRACT

The reactor neutron-capture cross section of 18-minute Rb^{88} has been determined by an activation method. The yield of Rb^{89} formed by successive neutron capture in Rb^{87} was determined by counting the beta rays emitted by its daughter, 51-day Sr^{89}. In these experiments Sr^{89} is also produced by the $Sr^{88}(n, \gamma)Sr^{89}$ reaction from the Sr^{88} contamination in the rubidium target and from Sr^{88} formed by the beta decay of Rb^{88}. Corrections for the contributions from these sources to the yield of Sr^{89} have been measured experimentally. The reactor neutron-capture cross section of Sr^{88} has been measured to be 5.8 mb. for the conditions of the experiment. Taking 0.12 ± 0.3 barn for the thermal cross section of Rb^{87}, the cross section of Rb^{88} was found to be 1.0 ± 0.3 barn for reactor neutrons.

INTRODUCTION

A measurement of the capture cross section of 18-minute Rb^{88} for reactor neutrons has been made using an activation method depending on successive neutron capture in Rb^{87}. Using the same technique Katcoff (1) set an upper limit of 200 barns for the thermal-neutron capture of Rb^{88}. With the advantage of much higher neutron flux than the one available to Katcoff, it has been possible to improve upon his measurement.

The following nuclear reactions occur when Rb^{87} is irradiated with neutrons:



The cross section of Rb^{88} was determined by measuring the Sr^{89}, daughter of Rb^{89}, which is formed by successive neutron capture in Rb^{87}.

According to the reactions listed above three processes lead to the formation of Sr^{89}. First, Sr^{89} can be formed from strontium impurity by neutron capture in Sr^{88}. The contribution of this first-order reaction to the observed yield of Sr^{89} can be determined experimentally by irradiating a sample at a low neutron flux so that the successive neutron capture in Rb^{87} is negligible. Then the formation of Sr^{89} from Sr^{88} in the higher flux irradiations is calculated from the measured cross section of Sr^{88} using the following equation:

$$[1] \qquad N_1 = (N_K \sigma_K \phi/\lambda)(1-e^{-\lambda t}),$$

where N_1 is the number of atoms of Sr^{89} at the end of the irradiation formed from strontium impurity,

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[2] *Present address: St. Augustine's Seminary, Toronto, Ontario.*

N_K is the number of atoms of Sr^{88} in the rubidium samples as determined by measurement at low neutron flux,
σ_K is the cross section of Sr^{88},
ϕ is the neutron flux,
t is the time of irradiation,
λ is the decay constant of Sr^{89}.

Secondly, Sr^{89} is formed by neutron capture in Sr^{88} formed by beta decay of Rb^{88} during the irradiation. The contribution of this process can be calculated using the following equation derived by Katcoff (2):

$$[2] \qquad N_2 = N_S\sigma_S\sigma_K\phi^2/\lambda^2\left[\lambda t-(1+T_A/T)(1-e^{-\lambda t})+\frac{T_A\lambda(e^{-\lambda_A t}-e^{-\lambda t})}{T(\lambda-\lambda_A)}\right],$$

where N_2 is the number of atoms of Sr^{89} at the end of the irradiation from Sr^{88} formed by beta decay of Rb^{88},

N_S is the number of atoms of Rb^{87} initially present,
σ_S is the neutron-capture cross section of Rb^{87}, taken to be 0.12 b. (3),
T_A is the half-life of Rb^{88}, taken to be 17.8 minutes (4),
T is the half-life of Sr^{89}, taken to be 51 days (5),
λ_A is the decay constant of Rb^{88}.

The other symbols have been defined under Eq. [1].

Thirdly, Sr^{89} is formed by the reaction under study: decay of Rb^{89} produced by successive neutron capture in Rb^{87}. The equation which describes this process is derived as follows: the time rate of change of Sr^{89}, dN_3/dt, is equal to its rate of production by beta decay from Rb^{89}, $\lambda_B N_B$, minus its natural disintegration rate, i.e.,

$$[3] \qquad dN_3/dt = \lambda_B N_B - \lambda N_3.$$

According to Ref. 2 N_B is given by:

$$[4] \qquad N_B = \frac{N_S\sigma_S\sigma_A\phi^2}{\lambda_A\lambda_B(\lambda_B-\lambda_A)}[\lambda_B(1-e^{-\lambda_A t})-\lambda_A(1-e^{-\lambda_B t})].$$

Substituting Eq. [4] in Eq. [3] and solving with $N_3 = 0$ at $t = 0$ gives:

$$[5] \qquad N_3 = \frac{N_S\sigma_S\sigma_A\phi^2}{\lambda_A(\lambda_B-\lambda_A)}\left[\frac{T(T_A-T_B)(1-e^{-\lambda t})}{T_AT_B}+\frac{T_AT(e^{-\lambda t}-e^{-\lambda_A t})}{T_B(T_A-T)}+\frac{T_BT(e^{-\lambda_B t}-e^{-\lambda t})}{T_A(T_B-T)}\right],$$

where N_3 is the number of atoms of Sr^{89} at the end of the irradiation, produced by decay of Rb^{89},

σ_A is the cross section to be measured,
T_B is the half-life of Rb^{89}, taken to be 14.9 minutes (6),
λ_B is the decay constant of Rb^{89}.

The other symbols have been defined under Eq. [1] and Eq. [2].

Equation [5] gives only the Sr^{89} present at the end of the irradiation. Another term should be added to take into account the formation of Sr^{89} from Rb^{89} by beta decay after the irradiation. This term is equal to N_B, the number of atoms of Rb^{89} present at the end of the irradiation, and is given by Eq. [4]. Therefore the Sr^{89} from beta decay of Rb^{89} is equal to N_3+N_B.

A re-evaluation of the neutron-capture cross section of Sr^{88} was made. A value of 5 ± 1 mb. has been reported by Seren *et al.* (7) for the thermal-neutron-capture cross

section of Sr^{88}, but considering the potential importance of the (n, γ) reaction on Sr^{88} in these experiments, this cross section was measured under conditions similar to those used in the measurement of the cross section of Rb^{88}.

A spectrographic analysis of the rubidium chloride showed that there was less than 0.02 p.p.m. of yttrium and zirconium. Therefore the formation of Sr^{89} by $Y^{89}(n, p)$ and $Zr^{92}(n, \alpha)$ processes on these two elements is ruled out.

EXPERIMENTAL

Samples of rubidium chloride were irradiated in the NRX reactor at Chalk River. The experimental conditions are given in Table I.

TABLE I

EXPERIMENTAL CONDITIONS USED FOR THE IRRADIATIONS

Experiment No.	RbCl irradiated (g.)	Irradiation time (hr.)	Neutron flux (n./cm.²/sec.)	Chemical yield (%)	Self-scattering* and self-absorption (%)
1	0.6375	16.5	6.57×10^{13}	77.0	+ 8.0
2	0.5922	16.3	6.37×10^{13}	84.2	+ 8.0
3	0.6366	16.5	6.64×10^{13}	40.2	+10.0
4	0.5528	108.8	7.83×10^{12}	53.6	+10.0
5	0.5298	109.8	3.25×10^{12}	67.9	+ 9.0

**The plus sign indicates that the net effect of self-scattering and self-absorption was an increase in the counting rate.*

The chemical purification was started about one month after the end of the irradiation. The rubidium samples were dissolved in 2–3 ml. of distilled water in the presence of 20 mg. of strontium carrier. Strontium nitrate was precipitated by addition of fuming nitric acid, centrifuged, washed with fuming nitric acid, and finally dissolved in a minimum amount of water in the presence of rubidium carrier. After this purification cycle was repeated four or five times, the strontium nitrate was dissolved in 6–8 ml. of water and several ferric hydroxide scavengings were made by addition of gaseous ammonia; the precipitates were discarded. The solution was then prepared for ion-exchange purification by precipitating strontium as carbonate. The precipitate was centrifuged and dissolved in the minimum amount of HCl, to which solution calcium and barium carriers and an equal volume of 1.5 *M* ammonium lactate were added. The solution was passed through Dowex-50 ion-exchange column using conditions similar to those described by Milton and Grummitt (8) for the separation of alkaline-earths using 1.5 *M* ammonium lactate as an eluant at pH 7. The strontium fraction was reduced in volume from 40 to 15 ml. and 2 ml. of 3 *N* sulphuric acid plus 2 ml. ethyl alcohol was added. This solution was allowed to stand overnight to let the strontium sulphate form and digest. The precipitate was centrifuged and washed with 1 ml. of water and ethyl alcohol. Finally it was transferred to a weighed aluminum counting tray, dried, weighed, and counted.

The disintegration rate of the strontium fraction was determined with an anthracene beta-counter having a window thickness of 2.16 mg./cm.² The counter was shielded with 4 inches of lead. The background was 9.7 c.p.m. and the variation during the interval over which the samples were counted was ±0.3 c.p.m. The counter efficiency was determined with a weightless source of P^{32}, mounted on an aluminum tray and prepared from a N.B.S. Standard. The efficiency found in this way was 32%. The

combined effects of self-scattering within the sources and self-absorption were determined in a separate experiment by the following method (9): To a thin layer of Sr^{89} activity, prepared by the $Sr^{88}(n, \gamma)Sr^{89}$ reaction, successive layers of inert strontium sulphate were added and the observed intensity was plotted against the weight of the inert material. The correction for self-scattering and self-absorption for a particular source thickness was then obtained from this curve after the amount of strontium sulphate present in each source was divided by two to take into account the homogeneous distribution of activity throughout the sources. The net effect was an increase in counting rates of about $9\pm3\%$.

RESULTS

Strontium-89 was identified by its maximum beta-ray energy and its decay period measured over two half-lives. The absorption curves in aluminum of the beta radiations of the activity found in experiments 1, 2, 3, and of Sr^{89}, prepared by (n, γ) reactions on strontium, were the same. A typical curve and the Sr^{89} standard curve are shown in Fig. 1. Fig. 2 shows the decay curves for the activities produced in two irradiations

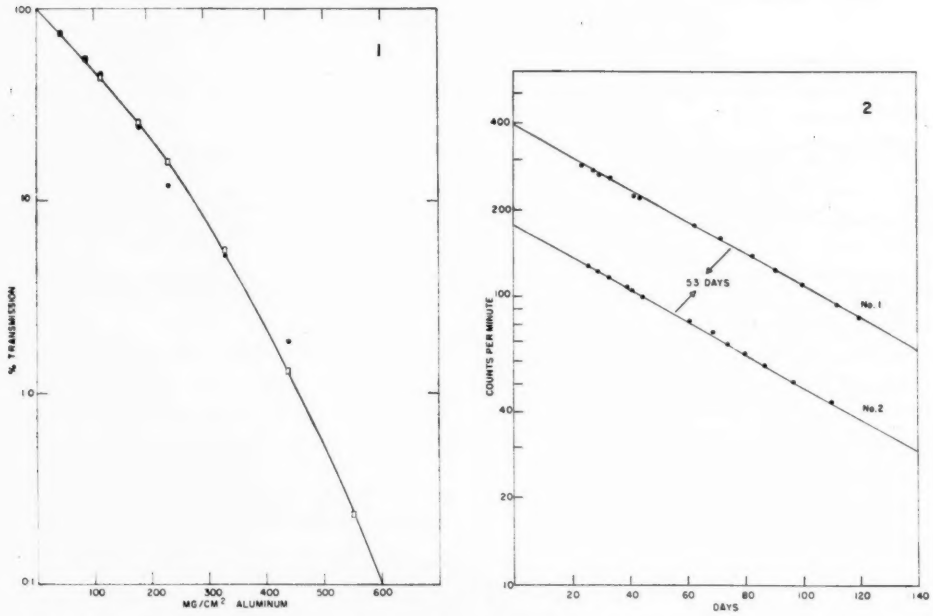

FIG. 1. Absorption curve of Sr^{89}; the circles are from the activity in the separated strontium, the squares are from a Sr^{89} standard prepared by a (n, γ) reaction in strontium.
FIG. 2. Decay curves of activities in experiments 1 and 2. The counting rates in experiment 1 have been multiplied by two.

done in a high neutron flux (expts. 1 and 2); the third one (expt. 3) is not included, because its decay has been measured for only 20 days. The measured value of the half-life in both experiments was 53 days, which, within the errors of the measurements, is in agreement with the value of 51 days for Sr^{89} (5). In experiments 4 and 5 done at low neutron flux a long-lived radioactive impurity amounting to 4 c.p.m. was found. After

this has been subtracted the remaining activity showed a 51-day half-life. This Sr^{89} activity arises mainly from neutron capture in Sr^{88} impurity present in the samples as described in the introduction.

The results are summarized in Table II. The observed counting rates were extrapolated to the end of the irradiation and absolute disintegration rates were obtained by making corrections for chemical yield, counting efficiency of the beta detector, and the combined effects of self-scattering and self-absorption within the sample.

TABLE II

NEUTRON-CAPTURE CROSS SECTION OF Rb^{88}

Experiment No.	Sr^{89} measured experimentally (dis./min.)	Sr^{89} due to Sr impurity λN_1 (dis./min.)	Sr^{89} calculated from Eq. 2 λN_2 (dis./min.)	Sr^{89} due to β decay of Rb^{89} $\lambda(N_3+N_B)$ (dis./min.)	σ_A Rb^{88} (barn)
4	209	156	23	30	
5	113	105	3	5	
1	724	320	40	364	0.96
2	608	286	34	288	0.88
3	787	323	41	423	1.1
				Average	0.98

The average value for the Sr^{88} present as an impurity in the irradiated rubidium was determined from experiments 4 and 5 to be $1.7\pm0.4\times10^{-6}$ part per atom of Rb^{87}. Its contribution to the formation of Sr^{89} was calculated using Eq. [1]. Likewise the contribution from neutron capture in Sr^{88}, formed by beta decay of Rb^{88} during the irradiation, was calculated using Eq. [2]. The contribution of these two processes, subtracted from the total activity measured in experiments 1, 2, and 3, gives the Sr^{89} formed by successive neutron capture in Rb^{87}.

The neutron flux in each experiment was determined by measuring the activity in a weighed piece of pure cobalt wire, 0.005 inch in diameter and 0.4 inch long, with an ionization chamber calibrated with standardized Co^{60} sources. A correction of 2.1% was applied to take into account the self-shielding of the cobalt wire (10). The reactor cross section of Co^{60} was calculated to be 36.6 barns, taking 36.0 ± 1.5 barns (3) for its thermal-neutron-capture cross section and 48.6 for its resonance integral (11). A value of 5.20 years (12) was taken for the half-life of Co^{60}.

By solving Eqs. [4] and [5] the cross section of Rb^{88} was obtained for each experiment and the results are given in Table II. The mean is 1.0 ± 0.25 barn. The limits of error of the measurements which contributed most to the quoted error are: $\pm20\%$ from the precision with which the amount of strontium impurity is known; $\pm7\%$ from the value of the neutron-capture cross section of Sr^{88}; $\pm8\%$ from the counting; and $\pm2\%$ for the neutron-flux determination. Combining these errors by the method of the square root of sum of squares type of addition, the resulting error in the mean value is ±0.25 barn. The assigned error of $\pm25\%$ in the value of the thermal-neutron cross section of Rb^{87} is not included in the error of the present measurement. The cross section refers to reactor spectrum neutrons, since no experiments were done to determine the epicadium contribution.

For the measurement of the neutron-capture cross section of Sr^{88} two weighed strontium carbonate samples were irradiated in two different neutron fluxes in the

NRX reactor. A few days after the end of the irradiation, the samples were dissolved in a minimum amount of dilute HCl and the volume made up to 10 ml. Weightless Sr^{89} sources were prepared for beta-counting by pipetting 50λ aliquots onto aluminum trays.

Counting and determination of the neutron flux were done by the technique described above. An absorption curve in aluminum showed the presence of a gamma component, due to 65-day Sr^{85}. This contribution amounted to 2.5% of the observed activity and was subtracted from it. Errors of 5% in the counting and of 2% in the neutron-flux determination were estimated.

The cross section was thus measured to be 5.8 ± 0.4 mb. for reactor neutrons; this is the average of the two, which agreed within 1%. Within the limits of errors quoted by Seren *et al.* (7), this value is in agreement with theirs.

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ALKYLGUANIDINE NITRATES AND ALKYLNITROGUANIDINES[1]

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ABSTRACT

The fusion of mixtures of alkylamine nitrates, $RR'NH.HNO_3$ ($R' = H$ when R = methyl, isopropyl, isobutyl, *n*-amyl, and phenyl, and $R' = C_2H_5$ when R = ethyl), and dicyandiamide, or calcium cyanamide, or calcium cyanamide and urea, yielded alkylguanidine nitrates. The latter were also obtained by heating solutions of alkylamine nitrates and calcium cyanamide. By treatment of the alkylguanidine nitrates with sulphuric acid, alkylnitroguanidines were prepared in good yields. A study of the effect of temperature on the yield of *n*-amyl and of time and temperature on the yields of methyl, isopropyl, and isobutyl nitroguanidine was made. The solubility of methyl, isopropyl, isobutyl, and *n*-amyl nitroguanidine in water and 10% and 20% sulphuric acid solutions at 0° C. was determined.

INTRODUCTION

Calculations based on the heat of combustion and on the empirical formula indicated that 1-methyl-3-nitroguanidine would be a more effective coolant than nitroguanidine in double base propellants. Since its density was satisfactory and it was relatively insoluble in the solvents and plasticizers used in propellant manufacture, further work was undertaken.

Davis (3) prepared alkylnitroguanidines by direct nitration of alkylguanidine sulphates in sulphuric acid and also by reacting nitroguanidine with alkylamines (2, 4). Yields were satisfactory but the preparation required nitroguanidine. McKay and Wright (6) improved this method by reacting alkylamine hydrochlorides with the potassium salt of nitroguanidine. The yield, however, did not exceed 70% based on nitroguanidine. When we consider that picrite is made in 55% yield from calcium cyanamide or 70% from dicyandiamide, the yield of alkylnitroguanidine could not be greater than 40–50%. Therefore other methods of producing this material should be considered. Methods described herein are based on calcium cyanamide, dicyandiamide, and alkylamine nitrates.

Werner and Bell (9) have stated that the fusion of dicyandiamide with alkylamine hydrochlorides gives a nearly quantitative yield of alkylguanidine hydrochlorides. This statement has been challenged by other investigators (7), who reported a yield in the order of 80%. Moreover, alkylguanidine hydrochlorides would not be of much value for the preparation of alkylnitroguanidine, since they would have to be converted into either the sulphate or the nitrate.

It was believed that methods employed to produce alkylguanidine nitrates from calcium cyanamide or dicyandiamide would give better yields if alkylamine nitrates were used in place of ammonium nitrate.

In the present work, alkylguanidine nitrates were synthesized from alkylamine nitrates and then converted into alkylnitroguanidines.

Alkylguanidine Nitrates

The alkylguanidine nitrates were synthesized by the fusion of alkylamine nitrates with

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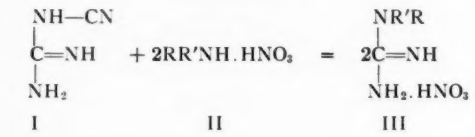
(*a*) dicyandiamide, (*b*) calcium cyanamide, and (*c*) calcium cyanamide and urea. They were also obtained by heating aqueous solutions of alkylamine nitrates and calcium cyanamide.

Alkylamine Nitrates and Dicyandiamide

The fusion of dicyandiamide with ammonium nitrate yielded guanidine nitrate. The reaction was mildly exothermic at 170° C. Similarly, when dicyandiamide and methylamine nitrate were fused together, an exothermic reaction took place at 170° C. but was less pronounced than in the previous case and was more easily controlled. Since alkylguanidine nitrates seemed stable in the fused state up to 190° C., when decomposition occurred, the reaction mixture, which became fluid at temperatures as low as 140° C., was maintained at a temperature of 170°–180° C. throughout the reaction.

By the reaction of 1 mole of dicyanamide (I) and 2 moles of alkylamine nitrate (II), 2 moles of alkylguanidine nitrate (III) were produced according to the following equation:



I II III

R′ = H when R = methyl, isopropyl, isobutyl, *n*-amyl, phenyl, and R′ = C_2H_5 when R = ethyl.

Alkylamine Nitrates and Calcium Cyanamide

The fusion of calcium cyanamide with ammonium nitrate has always been considered a hazardous process because of the high melting point of ammonium nitrate (170° C.) and its oxidizing properties when molten. However, when using alkylamine nitrates, which decomposed slightly at temperatures above 170° C., direct fusion of calcium cyanamide with alkylamine nitrates was considered practical.

By heating calcium cyanamide (55% pure) and alkylamine in a molar ratio of 1:3, alkylamines were evolved according to the following equation:

$$CaCN_2 + 3RR'NH.HNO_3 = RR'NC(NH)NH_2.HNO_3 + 2RR'NH + Ca(NO_3)_2.$$

Since calcium cyanamide contains approximately 20% of calcium oxide, more alkylamine was evolved:

$$CaO + 2RR'NH.HNO_3 = 2RR'NH + Ca(NO_3)_2 + H_2O.$$

An efficient recovery of the alkylamine evolved and of the unreacted alkylamine nitrate was necessary. Two methods were investigated in which calcium was discarded either as the carbonate or as the sulphate.

Calcium carbonate method.—By passing the alkylamine and carbon dioxide simultaneously into a solution of calcium nitrate at 60° C., precipitation of calcium carbonate commenced at pH 8.0. It was believed that calcium hydroxide was initially precipitated by alkylamine when pH 8.0 was reached:

$$Ca(NO_3)_2 + RR'NH = Ca(OH)_2 + RR'NH.HNO_3.$$

The carbon dioxide then reacted with calcium hydroxide:

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O.$$

After the calcium carbonate was removed, the filtrate was evaporated to dryness, leaving alkylamine nitrate.

Calcium sulphate method.—This method consisted in the absorption of alkylamine in dilute sulphuric acid to form alkylamine sulphate. The solution was then added to the filtrate containing calcium nitrate. Calcium sulphate was precipitated and the filtrate evaporated to dryness to yield alkylamine nitrate according to the equation:

$$(RR'NH_2)_2SO_4 + Ca(NO_3)_2 = 2RR'NH.HNO_3 + CaSO_4.$$

Alkylamine Nitrates, Calcium Cyanamide, and Urea

Urea was used successfully in the Wright (fusion) process (5, 10), where it acted as a melting-point depressant for ammonium nitrate. When urea was added to alkylamine nitrates, fusion could be carried out effectively with calcium cyanamide at 90° C.

Alkylamine Nitrates, Calcium Cyanamide, and Water

The process patented by Burns, Gay, and I.C.I. (1) makes use of an aqueous solution of ammonium nitrate and calcium cyanamide to produce guanidine nitrate. It was considered of interest to react alkylamine nitrates and calcium cyanamide in a similar manner. By heating aqueous solutions of alkylamine nitrates and calcium cyanamide, alkylamines were evolved as before but the yields of alkylguanidine nitrates, with the exception of phenylguanidine nitrate, were lower.

Alkylnitroguanidines

Alkylnitroguanidines, $RR'NC(NH)NHNO_2$, were prepared by treatment of alkylguanidine nitrates, $RR'NC(NH)NH_2.HNO_3$, with sulphuric acid. This reaction was believed to be a dehydration process in which 1 mole of water was removed from the alkylguanidine nitrate by sulphuric acid to form a hydrate or 85% sulphuric acid. However, in the case of nitroguanidine, it was found that the guanidine nitrate – sulphuric acid mixture is a nitrating mixture in which NO_2^+ ions are present (8). A similar mechanism is probably responsible for the formation of alkylnitroguanidine from alkylguanidine nitrate.

Of the six alkylguanidine nitrates studied, the phenyl- and diethyl-nitroguanidines could not be isolated. In the case of the phenylguanidine nitrate, nitroguanidine itself was isolated.

Since these alkylnitroguanidines were crystallized from dilute sulphuric acid solutions, the solubilities of these compounds in water and 10% and 20% sulphuric acid solutions at 0° C. were determined and were found to decrease with the increasing molecular weight.

A number of experiments were performed in order to show the effects of time and temperature on the yields of methyl, isopropyl, and isobutyl nitroguanidine. When the reaction time was arbitrarily set at 21 minutes, the most efficient temperature was found to be between 0° and 5° C. as indicated in Table II. The nitration of methylguanidine nitrate was found to be almost instantaneous at 40° C. when the time was limited to 5 minutes. However, this was not true in the cases of isopropyl and isobutyl guanidine nitrate where the best yields were obtained at 0° C. with a reaction time of 5 to 15 minutes as shown in Table III.

The degrading effect of the temperature over a reaction period of 1 hour is shown in Fig. 1 where the maximum yield of 91% of *n*-amylnitroguanidine at 0° C. decreases to a yield of 15% at 30° C.

EXPERIMENTAL

Alkylamine Nitrates

Dilute nitric acid was treated with an excess of the alkylamine. The solution was

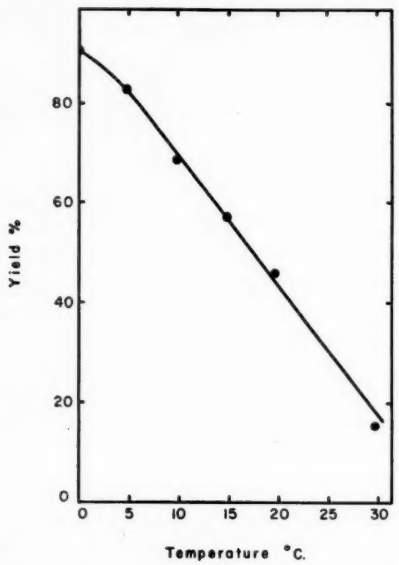


FIG. 1. Effect of temperature on the yield of *n*-amylnitroguanidine.

filtered and allowed to evaporate on a steam bath. In most cases the cooled product solidified.

Alkylguanidine Nitrates

The alkylguanidine nitrates were obtained by four different methods. The results in each case are given in Table I.

Alkylamine nitrates and dicyandiamide.—The alkylamine nitrate and dicyandiamide in a molar ratio of 2.1:1 were mixed together and heated on an oil bath. The fusion commenced at about 70° C. and the reaction mixture became clear at 135°–140° C. A temperature of 170°–180° C. was maintained for 3 hours. During this time a small amount of the alkylamine was evolved possibly owing to the decomposition of the slight excess of alkylamine nitrate employed. The reaction product, which solidified at about 35° C., was recrystallized from water.

Alkylamine nitrates and calcium cyanamide.—The alkylamine nitrate and calcium cyanamide in a molar ratio of 4:1 were mixed together and heated at 110° C. on an oil bath for 1 hour. Most of the alkylamine produced in the reaction was evolved during this time. About 40–50 ml. of hot distilled water was added to the flask and the mixture filtered while hot. In some cases more hot water was required. This necessitated the evaporation of the excess under vacuum. Finally when the solution was cooled to room temperature, the alkylguanidine crystallized, and it was recrystallized several times from water.

Alkylamine nitrates, calcium cyanamide, and urea.—The alkylamine nitrate, urea, and calcium cyanamide in a molar ratio of 4:3:1 were mixed together and heated at 90° C. for 1 hour. The alkylamine was evolved as before. The reaction products were treated with hot distilled water as described in the previous method.

Alkylamine nitrates, calcium cyanamide, and water.—An aqueous solution of alkylamine

TABLE I

ALKYLGUANIDINE NITRATES

Alkylguanidine nitrates $RR'NC(NH)NH_2.HNO_3$ R	R′	Starting materials		M.p., °C.	Yield, %	Formula	Calc., % HNO_3	Found, % HNO_3
CH_3	H	$CH_3NH_2.HNO_3$	+ 1*	149–150	79	$C_2H_5O_3N_4$	46.3	46.1
			2		88			
			3		77			
			4		—			
C_3H_7	H	$C_3H_7NH_2.HNO_3$	+ 1	119–121	72	$C_4H_{12}O_3N_4$	38.4	38.0
			2		71			
			3		44			
			4		39			
C_4H_9	H	$C_4H_9NH_2.HNO_3$	+ 1	83–84	88	$C_5H_{14}O_3N_4$	35.4	35.3
			2		92			
			3		56			
			4		43			
C_5H_{11}	H	$C_5H_{11}NH_2.HNO_3$	+ 1	71–72	71	$C_6H_{16}O_3N_4$	32.8	32.5
			2		70			
			3		43			
			4		36			
C_6H_5	H	$C_6H_5NH_2.HNO_3$	+ 1	125–126	47	$C_7H_{10}O_3N_4$	31.8	31.7
			2		63			
			3		75			
			4		73			
C_2H_5	C_2H_5	$(C_2H_5)_2NH.HNO_3$	+ 1	170–171	65	$C_5H_{14}O_3N_4$	35.4	35.0
			2		68			
			3		41			
			4		39			

*1 = $NH_2C(NH)NH.CN$; 2 = $CaCN_2$; 3 = $CaCN_2 + CO(NH_2)_2$; 4 = $CaCN_2 + H_2O$.

TABLE II

EFFECT OF TEMPERATURE ON THE YIELDS

Temp., °C.	Starting material	Yield	
		Crude, g.	Corrected, %
0	$CH_3NHC(NH)NH_2.HNO$ (13.6 g.) and 98% H_2SO_4 (40.8 g.)	8.5	94
5		9.2	100
15		8.9	97
30		8.3	92
0	$C_3H_7NHC(NH)NH_2.HNO_3$ (5 g.) and 98% H_2SO_4 (26.0 g.)	3.3	90
5		3.2	88
10		2.9	81
25		2.9	81
0	$C_4H_9NHC(NH)NH_2.HNO_3$ (5 g.) and 98% H_2SO_4 (26.0 g.)	3.1	82
5		2.7	73
10		2.6	69
30		2.1	58

nitrate (0.29 mole) in 100 ml. of water was heated until it reached a boiling point of 100° C. Calcium cyanamide (0.07 mole) was added slowly with stirring and the reaction was continued until there was no further evolution of the alkylamine. The mixture was filtered while hot and the alkylguanidine nitrate crystallized from the cooled filtrate.

Alkylnitroguanidines

Sulphuric acid (98%) was cooled to 0° C. and alkylguanidine nitrate was added slowly

TABLE III

EFFECT OF THE REACTION TIME ON THE YIELDS

Reaction temp., °C.	Time, min.			Yield	
	Addition	Stirring	Reaction	Crude, g.	Corrected, %
$CH_3NHC(NH)HN_2.HNO_3$ (13.6 g.) and 98% H_2SO_4 (40.8 g.)					
40	2.5	0.0	1.25	8.7	96
40	2.0	4.0	5.0	9.2	100
40	2.0	10.0	11.0	8.2	92
40	2.0	20.0	21.0	7.6	86
$C_3H_7NHC(NH)NH_2.HNO_3$ (5 g.) and 98% H_2SO_4 (26 g.)					
0	2.0	1.0	1.5	1.3	45
0	2.0	5.0	6.0	3.3	90
0	2.0	10.2	11.2	3.3	90
0	2.0	15.1	16.1	3.3	90
0	2.0	25.4	26.4	3.3	90
5	2.0	0.0	1.0	2.9	81
5	2.0	5.0	6.0	2.8	79
5	2.0	10.0	11.0	2.9	81
5	2.0	15.0	16.0	3.2	88
5	2.0	25.0	26.0	2.9	81
10	2.0	0.0	1.0	3.0	79
10	2.0	5.0	6.0	2.8	79
10	2.0	10.0	11.0	2.8	79
10	2.2	15.0	16.1	2.8	79
10	2.0	25.0	26.0	2.7	77
15	2.0	0.0	1.0	2.5	72
15	2.0	5.0	6.0	2.8	79
15	2.0	10.0	11.0	2.5	72
15	2.0	15.0	16.0	2.5	72
15	2.0	25.0	26.0	2.3	67
25	2.0	0.0	1.0	2.4	70
25	2.0	5.0	6.0	3.1	88
25	2.0	10.0	11.0	3.1	85
$C_3H_7NHC(NH)NH_2.HNO_3$ (5 g.) and 98% H_2SO_4 (26 g.)					
25	2.0	15.2	16.1	3.0	83
25	2.0	25.0	26.0	2.8	79
$C_4H_9NHC(NH)NH_2.HNO_3$ (5 g.) and 98% H_2SO_4 (26 g.)					
0	2.0	0.0	1.0	2.3	65
0	2.0	5.0	6.0	2.6	71
0	2.0	10.0	11.0	3.6	84
0	2.0	14.9	16.0	3.4	89
0	2.1	24.9	25.9	3.3	87
5	2.5	0.0	1.3	2.5	67
5	2.0	5.2	6.2	2.6	71
5	2.0	10.0	11.0	2.6	71
5	1.9	15.3	16.2	2.6	71
5	2.1	25.0	26.0	2.6	71
10	2.0	0.0	1.0	2.5	67
10	2.0	5.1	6.1	3.2	82
10	2.1	10.0	11.0	3.2	82
10	2.2	16.1	17.2	3.2	82
10	2.1	25.0	26.0	2.7	71
20	2.1	0.0	1.0	2.0	56
20	2.0	5.7	6.7	2.4	64
20	2.0	10.0	11.0	2.2	60
20	1.9	15.1	16.1	2.1	58
20	2.0	25.0	26.0	2.1	58
30	2.3	0.0	1.2	2.2	62
30	1.9	5.1	6.1	2.1	58
30	2.0	10.1	11.1	1.9	56
30	2.0	15.0	16.0	2.3	64
30	2.1	25.0	26.0	2.1	58

with stirring and cooling. After all the solid material had been added, the mixture was stirred at this temperature for 21 minutes and then poured over cracked ice. A white solid precipitated out of the diluted acid solution and was recrystallized from water. The crude yields and the yields corrected for solubility are given in Table II in grams and per cent respectively for methyl, isopropyl, and isobutyl nitroguanidine. When *n*-amylguanidine nitrate was used, the reaction time was arbitrarily set at 1 hour. The results obtained are shown in Fig. 1.

Studies were also made of the effect of the reaction time on the yields of methyl, isopropyl, and isobutyl nitroguanidines at various temperatures. The reaction time was taken as half of the addition time plus the stirring time. The results are given in Table III.

Solubility Determinations

An accurately weighed quantity of the alkylnitroguanidine was added to 50 ml. of distilled water. The solution was cooled to 0° C. and maintained at this temperature for 24 hours. After it had been filtered on a sintered glass crucible, the residue was dried over calcium chloride in a vacuum disiccator for 8 days. The weight of the insoluble material remaining as residue was subtracted from the original weight and the solubility was calculated.

The same procedure was used to determine the solubility of the alkylnitroguanidine in 10% and 20% sulphuric acid solutions. In these cases the residue was washed with a saturated solution of the alkylnitroguanidine after filtration.

The solubilities in grams at 0° C. in 100 g. of water and 10% and 20% sulphuric acid solutions for the different nitroguanidines were, respectively:

methyl —0.704, 0.977, and 1.29; isopropyl—0.502, 0.528, and 1.70;
isobutyl—0.483, 0.528, and 1.70; *n*-amyl—0.128, 0.110, and 0.13.

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ELECTROLYTIC CONDUCTANCE IN HYDROGEN PEROXIDE – WATER MIXTURES

PART II. SOME MONOBASIC AND DIBASIC ACIDS[1]

D. K. THOMAS[2] AND O. MAASS

ABSTRACT

Measurements of the equivalent conductance of sulphuric, nitric, and hydrofluoric acids were made in water – hydrogen peroxide mixtures by means of a direct-current method. It was found that in solvents containing a high percentage of hydrogen peroxide the conductivities of these acids were extremely low, and it is proposed that this results from a marked decrease in their degrees of dissociation. This proposal is supported by similar measurements made on the system water – strong acid – weak acid.

INTRODUCTION

As stated in a previous communication (1), measurements of the conductance of acids such as sulphuric and nitric in hydrogen peroxide – water mixtures (2) show that their values are considerably lower than those in aqueous solution. When the composition of the solvent is of the order of 90% to 100% hydrogen peroxide, Shanley *et al.* (2) found that when the composition of the solvent is of the order of 99% to 100% H_2O_2, sulphuric acid possesses a lower conductance than its potassium salt. They regarded the reduced conductance of the acid as being due partly to a decrease in the second dissociation step of HSO_4^- to H^+ and $SO_4^=$. The further suggestion was made that the solvated proton $H^+.H_2O_2$ showed a chain conductance in anhydrous hydrogen peroxide which was greatly reduced in the presence of water.

In the present work three acids, namely sulphuric, nitric, and hydrofluoric, have been studied at a few temperatures in solvents of composition ranging from 0 to 98 weight % of hydrogen peroxide.

EXPERIMENTAL PROCEDURE

The conductance measurements were carried out in exactly the same way as those in Part I; for the measurements on solutions of hydrofluoric acid a specially constructed Teflon cell was employed. The tin probe electrodes and current-carrying electrodes were found to be suitable for use in solutions of the concentration encountered in this work. As before, all solutions were made up by weight from the pure constituents and measurements were made with the cell immersed in a thermostat controlled to $\pm 0.01°$ C.

MATERIALS

(*i*) *Hydrogen peroxide.*—Becco chemicals 98% hydrogen peroxide was used throughout, and dilution was carried out with water of specific conductance 1.5×10^{-6}.

(*ii*) *Acids.*—The sulphuric, nitric, and hydrofluoric acids employed were all of analytical grade, the amount of metallic and other impurity being less than 0.0001%.

RESULTS

The results for the three systems studied are shown in Table I A (sulphuric acid), B (nitric acid), and C (hydrofluoric acid). The extrapolated values of Λ_0 are also given. In Fig. 1 the data of Shanley *et al.* (2) (called Becco a-c. results on the figure) for the

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TABLE I

VALUES OF Λ FOR THREE SYSTEMS AT 25°, 16°, 10° C. AND 0, 31, 78, 98 WT. % H_2O_2

$C^{\frac{1}{2}}$	25° C.				16° C.				10° C.			
	0	31	78	98	0	31	78	98	0	31	78	98
					A. System H_2SO_4–H_2O_2–H_2O							
0.020	414.8	246.0	103.0	42.0	—	207.0	94.2	37.0	—	186.0	82.0	34.5
0.050	385.0	233.0	93.0	41.2	—	198.7	86.6	35.8	—	180.0	77.5	34.0
0.075	360.2	221.2	85.6	40.5	—	191.6	80.6	35.0	—	174.0	73.0	32.7
0.100	338.4	210.0	79.8	40.0	—	184.5	75.0	34.6	—	168.5	68.5	32.0
0.150	301.2	191.0	71.7	38.4	—	170.5	63.0	33.8	—	158.0	59.6	30.0
0.200	272.0	178.0	65.0	37.0	—	156.0	—	33.0	—	146.0	51.0	29.0
Λ_0	434.2	256.0	109.6	42.5	375.0	213.0	98.7	38.2	338.0	191.0	86.0	36.0
					B. System HNO_3–H_2O_2–H_2O							
0.020	416.0	243.0	104.0	58.0	—	207.2	91.0	52.6	—	184.5	82.5	50.0
0.050	412.0	241.0	103.0	52.0	—	205.0	89.5	47.5	—	183.5	81.5	45.0
0.075	409.0	239.0	102.0	47.0	—	203.0	88.5	43.0	—	182.2	80.5	40.5
0.100	405.0	237.0	101.3	42.0	—	201.0	87.2	38.8	—	181.2	79.8	36.0
0.150	399.0	233.2	100.0	32.0	—	197.0	85.0	30.0	—	179.0	78.0	27.2
0.200	393.0	230.0	98.0	23.0	—	—	83.0	20.6	—	177.0	76.0	19.0
Λ_0	418.5	244.0	105.0	62.0	362.0	209.0	92.0	56.0	326.0	185.0	83.0	54.0
					C. System HF–H_2O_2–H_2O							
0.05	137.0	111.0	21.0	4.5					109.0	77.0	20.0	3.5
0.10	93.0	65.0	17.3	1.8					85.0	55.5	14.0	1.2
0.20	57.0	36.5	14.5	1.4					54.0	33.8	8.8	1.0
0.30	40.0	29.0	13.0	1.1					38.7	24.2	7.4	1.0
0.40	31.0	24.0	11.5	1.0					30.0	19.5	6.5	0.8
0.50	28.0	22.0	11.0	0.7					25.0	16.3	6.2	0.4

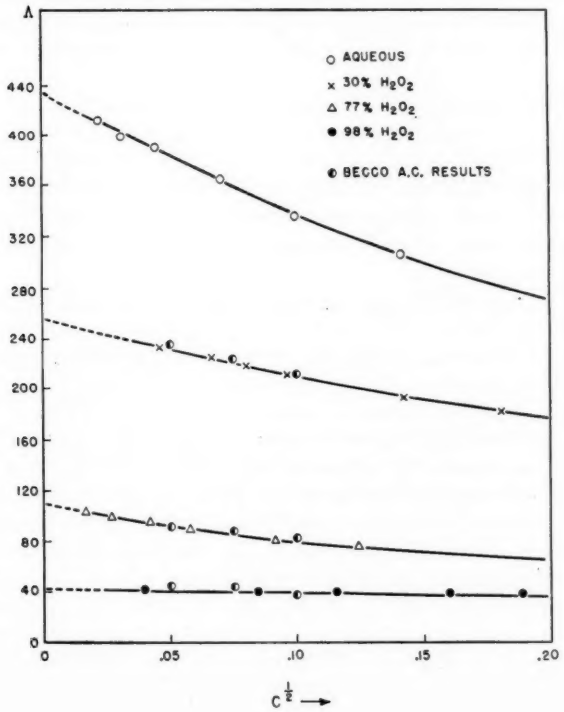


FIG. 1.

system H_2SO_4–H_2O–H_2O_2 are plotted together with the results of the present work on the same system, and this serves to demonstrate the measure of agreement attainable between the two experimental techniques.

DISCUSSION

It is of interest to record the variation in conductivity with temperature in H_2O_2–H_2O–electrolyte systems. In Table II are given such data using the relationship $\Lambda T_0 = \Lambda_{25}[1+x(T-25)]$.

TABLE II

VARIATION IN Λ WITH TEMPERATURE OVER THE RANGE 10° C. TO 25° C.

Wt. % H_2O_2	HNO_3	H_2SO_4
0	0.0145	0.0150
31	0.0161	0.0169
78	0.0134	0.0144
98	0.0086	0.0063

In Table I A, B, and C the solute concentration (C) is expressed in g-equiv. per liter, and the values quoted are equivalent conductances corrected for the solvent conductance.

The results presented in Table I A, B, and C possess one feature in common, namely that an increase in the weight % of hydrogen peroxide greatly reduces the equivalent conductance of the system H_2O–acid–H_2O_2, and in the case of almost anhydrous hydrogen peroxide the conductance has a value which is an order of magnitude less than that in aqueous solution.

Now the exceptional mobility of the proton in aqueous solution is attributed to a special mechanism of transport known as 'chain conductance'. This is made possible by the nature of the solvent itself, and requires that (*a*) the solvent molecules should possess an affinity for protons and (*b*) they should form a three-dimensional hydrogen-bonded network in the liquid state. In general, therefore, we should expect hydroxylic solvents such as the alcohols, glycols, and hydrogen peroxide to be able to sustain this 'chain conductance' process.

In the liquid state it is certain that hydrogen peroxide and water have very similar structures, both being highly associated through intermolecular hydrogen-bonding. The magnitude of the frequency shifts (3) observed in the infrared absorption spectra of the two compounds suggests that the hydrogen bond formed in hydrogen peroxide is somewhat stronger than that formed in water. Furthermore, evidence from a number of properties such as heat of mixing (4), vapor pressure (5), density (6, 7), viscosity (8, 9), and dielectric constant (10) indicates that the number, or force, of attractions increases upon the addition of the former to the latter. In other words, hydrogen bonds between water and hydrogen peroxide molecules are more stable than those between molecules of the pure substances. Thus hydrogen peroxide, which is capable of participating in twice as many intermolecular hydrogen bonds as is water, would have the effect of 'tightening' the structure of the latter, and one might anticipate that the proton mobility in H_2O–H_2O_2 mixtures would be as great as that in pure water. The fact that this supposition is so greatly at variance with the experimental results may be due to two things:

(*a*) the chain-conductance process is no longer occurring in anhydrous hydrogen peroxide and addition of peroxide to the water–acid system brings about a gradual breakdown in this process, and/or

(*b*) the number of ions present in the solution is greatly decreased as the result of a reduction in the degree of dissociation of the acid.

In view of the similarity which has been established between the liquid structures of pure water, pure hydrogen peroxide, and mixtures of the two, suggestion (*a*) above is hardly likely to be true, and an explanation of the experimental results must be sought principally in terms of effect (*b*).

The extent to which an acid will dissociate in solution is determined by the basic nature of the solvent and its dielectric properties. Referring again to pure water and almost anhydrous hydrogen peroxide, we find that the difference in dielectric constant is small but that there is an appreciable difference in their relative acidities. Measurements of the pH of mixtures of H_2O–H_2O_2 have been made and, although data from different sources (11, 12) do not agree well (see Fig. 2), they all show that the acidity increases considerably with percentage H_2O_2.

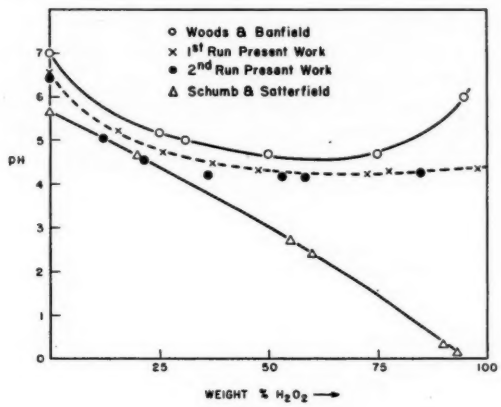


FIG. 2.

In the system H_2O–acid–H_2O_2 the following equilibria are possible:

(i) $HA + H_2O \rightleftharpoons H_3O^+ + A^-$,

(ii) $HA + H_2O_2 \rightleftharpoons H_3O_2^+ + A^-$,

(iii) $H_3O_2^+ + H_2O \rightleftharpoons H_3O^+ + H_2O_2$.

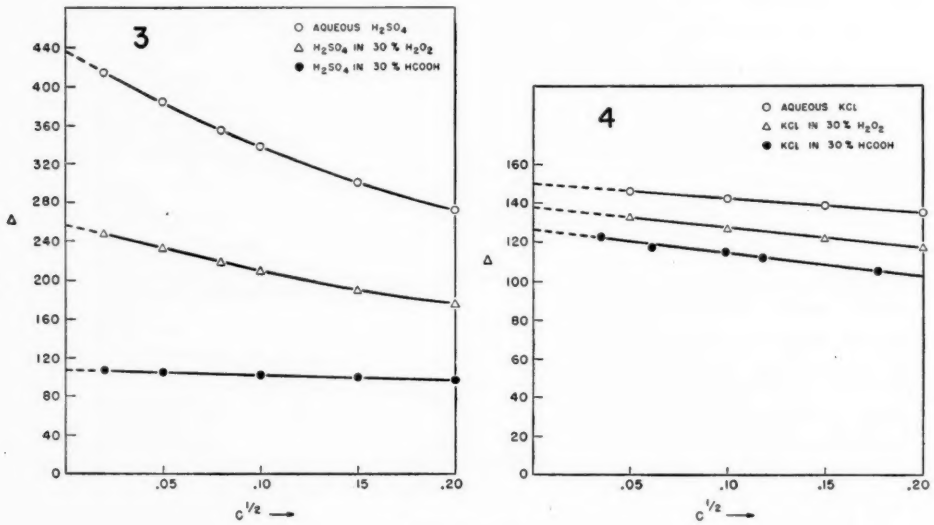
In case (i) when HA is a strong acid, the equilibrium will lie far to the right owing to the affinity of the water molecule for protons. As the basicity of the solvent molecule decreases, so too will the stability of the corresponding oxonium ion, and it is for this reason that the equilibrium position in (ii) lies well to the left. An independent measure of the relative stabilities of H_3O^+ and $H_3O_2^+$ has been given by Uri and Evans (13), who estimated a ΔH value of 4.2 kcal. per mol. for process (iii); thus assuming the entropy change to be small they find $\Delta G^\circ \simeq \Delta H^\circ = -4.2$ kcal., which gives an equilibrium constant of $K \simeq 10^3$.

As the concentration of H_2O_2 increases with respect to that of H_2O the number of ions produced by process (i) will decrease and become a minimum in almost anhydrous

hydrogen peroxide. This addition of H_2O_2 will bring about a gradual reduction in the equivalent conductance of the system, and the form of the pH curve suggests that the decrease will be most rapid for additions up to 30 weight %. Furthermore, although the degree of dissociation decreases, the mechanism of conductance remains the same as in aqueous solution, and so the temperature coefficients of conductances should also remain unchanged (except for a small change due to the effect on the dissociation constant).

These suppositions are in good agreement with the experimental results for the acids studied, and the very different behavior displayed by the alkali chlorides (1) in identical solvents adds strength to these opinions. If this is indeed a true picture of what is occurring, then similar effects should be observed in mixtures of water and any other weakly acidic substance. Conductivity measurements were therefore made in aqueous formic acid. Formic acid possesses both weakly acidic properties and a reasonably high dielectric constant (14). (It was because of its low dielectric constant that acetic acid was not used.) The effect of the reduced dielectric constant of H_2O–HCOOH mixtures as compared with that of H_2O–H_2O_2 mixtures can be assessed by measuring the conductance of KCl in a solvent of the same composition.

The results obtained are shown graphically in Figs. 3 and 4, and do indeed show that H_2SO_4 gives an over 100% lower conductance in H_2O–HCOOH than in H_2O–H_2O_2 mixtures. This would be expected from the greater acidity of HCOOH compared with H_2O_2. The results for KCl show that it behaves very much as it did in H_2O–H_2O_2 mixtures, the 7% lower values probably being due to the lower dielectric constant of the solvent.



FIGS. 3 and 4.

CONCLUSION

Abnormally low values are observed for the conductance of strong acids in water – hydrogen peroxide mixtures, the value being a minimum in almost anhydrous hydrogen

peroxide. An explanation is given in terms of a decrease in the degree of dissociation of these acids with increase in concentration of hydrogen peroxide in the solvent.

The proposals made were verified by conductance measurements on sulphuric acids and potassium chloride in water – formic acid mixtures.

ACKNOWLEDGMENTS

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SEVEN- AND EIGHT-MEMBERED RINGS CONTAINING CARBON AND TWO SULPHUR ATOMS[1]

MARSHALL KULKA

ABSTRACT

7-Chloro-2,3-dihydrobenzo(*f*)-1,4-dithiepin (IV) has been synthesized from 2-(2-chloroethylmercapto)-5-chlorobenzyl chloride (I). Attempts to synthesize the higher homologues of IV by this method failed because the required intermediates cleaved at the alkyl–sulphur bond. A reaction product of *p*-chlorothiophenol, formaldehyde, and hydrogen chloride has been identified as 2,8-dichloro-6H,12H-dibenzo(*b*,*f*)-1,5-dithiocin (VI), a tricyclic system with the eight-membered ring containing two sulphur atoms.

It has been previously shown (1, 2) that *o*-ω-chloroalkoxybenzyl isothiuronium chlorides (II, Y = O) undergo simultaneous degradation and cyclization in the presence of dilute alkali to form macrorings IV (Y = O) containing carbon, oxygen, and sulphur. It was also indicated that this reaction involves the intermediate III (Y = O). The ease with which these macrorings formed was attributed to the presence of the two heteroatoms which provided favorable bond angles.

In the present investigation it was decided to examine the preparation of rings containing two sulphur atoms. Accordingly *p*-chlorophenyl 2-chloroethyl sulphide was chloromethylated and the resulting 2-(2-chloroethylmercapto)-5-chlorobenzyl chloride (I, Y = S, $n = 2$) was treated with thiourea. This produced the required isothiuronium salt II (Y = S, $n = 2$) which when added to a large volume of hot dilute alkali yielded 7-chloro-2,3-dihydrobenzo(*f*)-1,4-dithiepin (IV, Y = S, $n = 2$). Attempts to synthesize the higher homologues of IV (Y = S, $n > 2$) failed because the required intermediates I (Y = S, $n > 2$) could not be obtained.

It was found that the sulphur–alkyl linkage of p-$ClC_6H_4S(CH_2)_nCl$ (where $n > 2$), unlike the ether linkage of p-$ClC_6H_4O(CH_2)_nCl$, was susceptible to cleavage under the acidic conditions of chloromethylation. Thus when *p*-chlorophenyl 4-chlorobutyl sulphide was subjected to the same chloromethylation conditions as were used in the preparation of 2-(2-chloroethylmercapto)-5-chlorobenzyl chloride (I, Y = S, $n = 2$) from *p*-chlorophenyl 2-chloroethyl sulphide, no reaction occurred. However, when the amount of condensing agent (zinc chloride) was increased, reaction did occur but I (Y = S, $n = 4$) was not the product. Instead, a high-melting, difficultly soluble compound was isolated. This compound was also formed when *p*-chlorothiophenol, bis(*p*-chlorophenylmercapto)-methane (3, 4), 1,2-bis(*p*-chlorophenylmercapto)ethane, and 1,4-bis(*p*-chlorophenylmercapto)butane but not 1,3-bis(*p*-chlorophenylmercapto)-2-chloropropane (5) were subjected to the more drastic chloromethylation. It became evident that *p*-chlorothiophenol was the intermediate in the formation of the high-melting compound and that the sulphides produced this intermediate by cleavage at the sulphur–alkyl bond. That 1,3-bis(*p*-chlorophenylmercapto)-2-chloropropane did not undergo cleavage under the acidic conditions of chloromethylation may be attributed to the steric hindrance offered by the alkyl chlorine atom. It is remarkable that bis(*p*-chlorophenyl) disulphide also remained unaltered under these conditions.

The structure of the unknown high-melting compound obtained from *p*-chlorothiophenol was determined in the following manner. Analyses revealed the empirical

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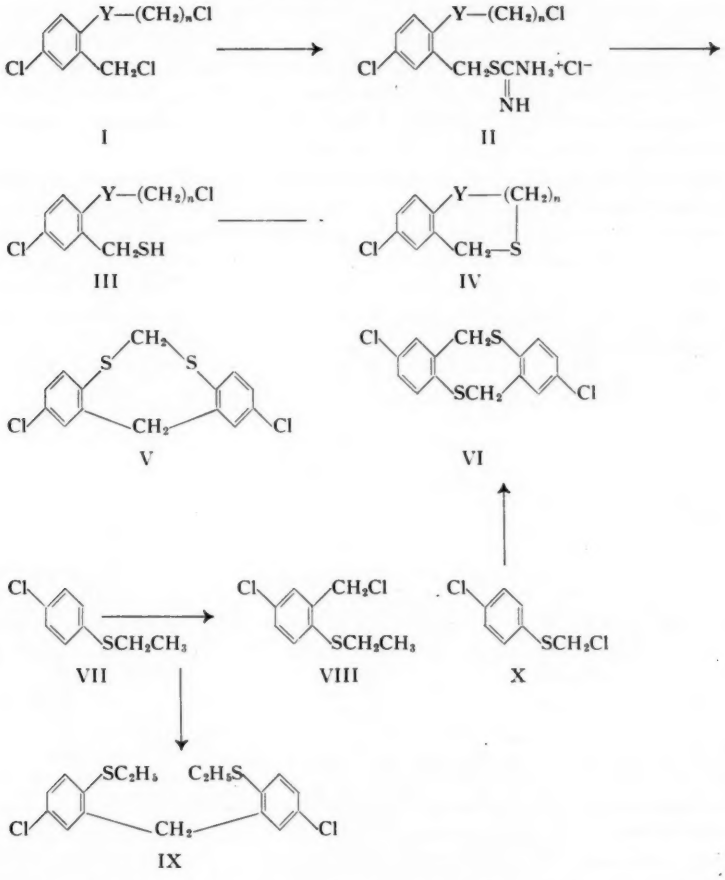
Contribution from the Dominion Rubber Company Limited Research Laboratories, Guelph, Ontario.



formula $C_{14}H_{10}Cl_2S_2$. A low molecular weight was indicated from the fact that the compound could be sublimed *in vacuo*, and a determination according to the method of Rast gave a figure of 315. On the basis of the properties and the origin of the compound, two possible structures, V and VI, were proposed. Further examination of the unknown compound showed that it was stable under a variety of acidic conditions and this finding eliminated the structure V, which is a mercaptal and therefore susceptible to acid hydrolysis. An attempt to synthesize V by preparing 2,2′-bis(ethylmercapto)-5,5′-dichlorodiphenylmethane (IX) from VII and VIII and subjecting it to chloromethylation resulted only in resinous material.

There are two possible routes by which the compound of structure VI could form from *p*-chlorothiophenol, formaldehyde, and hydrogen chloride in the presence of zinc chloride. Firstly, C-chloromethylation could occur to form 2-mercapto-5-chlorobenzyl chloride, two molecules of which could then react with each other in the presence of zinc chloride to form VI. Secondly, S-chloromethylation could occur to form *p*-chlorophenyl chloromethyl sulphide (X), two molecules of which could then undergo a Friedel–Crafts reaction with each other to form VI. That VI was formed via the second route was shown

by synthesis. *p*-Chlorothiophenol was treated with formaldehyde and hydrogen chloride according to the method of Scherer and Fink (6) to form *p*-chlorophenyl chloromethyl sulphide (X). Then when X was heated with zinc chloride in acetic acid 2,8-dichloro-6H,12H-dibenzo(*b*,*f*)-1,5-dithiocin (VI) was formed in high yield. On the other hand 2-ethylmercapto-5-chlorobenzyl chloride (VIII) when heated with zinc chloride in acetic acid saturated with hydrogen chloride did not produce VI.

The reaction of *p*-chlorothiophenol with formaldehyde and hydrogen chloride follows a course unlike that of its oxygen analogue. Thus when *p*-chlorophenol was treated with formaldehyde and hydrogen chloride under the conditions used in the preparation of VI, there was formed 6-chloro-8-chloromethyl-1,3-benzodioxane (7). This is obviously a reaction product of only one molecule of *p*-chlorophenol. *p*-Thiocresol did not produce a dithiocin of the type VI when subjected to chloromethylation. The product was a resin.

The chloromethylation of *p*-chlorothiophenol now provides an easy access to the ring system VI, which up to the present time was available only in the form of dibenzo(*b*,*f*)-1,5-dithiocin-6,12-dione, a dehydration product of thiosalicylic acid (8).

EXPERIMENTAL

2-(2-Chloroethylmercapto)-5-chlorobenzyl Chloride (*I*, $Y = S$, $n = 2$)

A reaction mixture of acetic acid (300 ml.), paraformaldehyde (10 g.), zinc chloride (15 g.), and 2-chloroethyl *p*-chlorophenyl sulphide (60 g.) (5) was saturated with hydrogen chloride and then heated at 85°–90° for 3 days. The reaction mixture was concentrated *in vacuo* to about half its original volume and then diluted with dilute hydrochloric acid. The precipitated oil was extracted with benzene, the benzene solution washed with water, with aqueous sodium bicarbonate, and with water. The solvent was removed and the residue fractionally distilled. Fraction 1, b.p. (12 mm.) = 150°–170°, 20 g.; fraction 2, b.p. (12 mm.) = 170°–185°, 13 g.; and fraction 3, b.p. (12 mm.) = 185°–190°, 25 g. Fraction 3, which was the required product, was not purified but was used directly in the formation of the isothiuronium salt (see below).

2-(2-Chloroethylmercapto)-5-chlorobenzyl Isothiuronium Chloride (*II*, $Y = S$, $n = 2$)

A solution of crude 2-(2-chloroethylmercapto)-5-chlorobenzyl chloride (fraction 3 above) (20 g.), thiourea (10 g.), and ethanol (120 ml.) was heated under reflux for 3 hours. The solvent was removed *in vacuo*, the residue dissolved in hot water (50 ml.), and the solution was allowed to cool. The white precipitate (15 g.) was filtered, washed with cold water and with benzene, and crystallized from water, yielding white prisms melting at 143°–145°. Anal. Calc. for $C_{10}H_{13}N_2Cl_3S_2$: C, 36.20; H, 3.92. Found: C, 36.01; H, 4.04.

7-Chloro-2,3-dihydrobenzo(f)-1,4-dithiepin (*IV*, $Y = S$, $n = 2$)

A solution of 2-(2-chloroethylmercapto)-5-chlorobenzyl isothiuronium chloride (8 g.) in methanol (50 ml.) and water (50 ml.) was added dropwise to a stirred hot solution of sodium hydroxide (5 g.) in water (500 ml.) heated on the steam bath. The addition time was approximately ½ hour and the reaction mixture was heated for an additional ½ hour. The precipitated yellow oil was extracted with benzene, the solution washed with water, and the solvent removed. The residue distilled at 180°–182° (12 mm.) and the distillate when crystallized from methanol yielded golden prisms (1.9 g. or 35%) melting at 91°–92°. Anal. Calc. for $C_9H_9ClS_2$: C, 49.87; H, 4.14. Found: C, 50.23, 49.96; H, 4.15, 3.94.

p-Chlorophenyl 4-Chlorobutyl Sulphide

To a solution of potassium hydroxide (30 g.) in methanol (100 ml.) was added *p*-chlorothiophenol (73 g.) and 1,4-dichlorobutane (300 ml.), and the resulting reaction mixture

was heated on the steam bath for ½ hour. There was a slight exothermic reaction at the beginning. Water was added to dissolve the precipitated salt and the organic layer was washed with aqueous alkali and with water. The excess 1,4-dichlorobutane was removed *in vacuo* and the residue was distilled, yielding a colorless liquid (92 g.) boiling at 180° (12 mm.), n_D^{20} = 1.5793. Anal. Calc. for $C_{10}H_{12}Cl_2S$: C, 51.07; H, 5.11. Found: C, 51.58; H, 5.27.

The residue from the distillation when crystallized from methanol gave white prisms of *1,4-bis(p-chlorophenylmercapto)butane* (6 g.) melting at 73°–74°. Anal. Calc. for $C_{16}H_{16}Cl_2S_2$: C, 55.98; H, 4.67. Found: C, 55.74; H, 4.48.

2,8-Dichloro-6H,12H-dibenzo(b,f)-1,5-dithiocin (*VI*)

(*a*) *From p-chlorothiophenol.*—A reaction mixture of *p*-chlorothiophenol (50 g.), zinc chloride (40 g.), paraformaldehyde (20 g.), and acetic acid (350 ml.) was saturated with hydrogen chloride and then heated on the steam bath for 16 hours. The resulting white precipitate was filtered from the cooled reaction mixture, washed with acetic acid, with concentrated hydrochloric acid, and with water, and dried. The crude product (35 g.) melted at 244°–246° and was insoluble in most organic solvents. When crystallized from benzene or N,N-dimethylformamide it melted at 254°–255°. Its melting point was not depressed by the products obtained in (*b*) or (*c*) (see below). Anal. Calc. for $C_{14}H_{10}Cl_2S_2$: C, 53.68; H, 3.19; Cl, 22.70; S, 20.45. Found: C, 53.87, 53.41; H, 2.92, 3.12; Cl, 23.37; S, 20.66, 20.85.

(*b*) *From sulphides.*—When bis(*p*-chlorophenylmercapto)methane (3, 4), 1,2-bis(*p*-chlorophenylmercapto)ethane (5), and 1,4-bis(*p*-chlorophenylmercapto)butane were subjected to chloromethylation as in (*a*) in each case a product was obtained melting at 254°–255° alone or in admixture with the 2,8-dichloro-6H,12H-dibenzo(*b,f*)-1,5-dithiocin (VI) obtained in (*a*).

(*c*) *From p-chlorophenyl chloromethyl sulphide* (*X*).—A solution of *p*-chlorophenyl chloromethyl sulphide (X) (6) (5 g.) in acetic acid (50 ml.) and zinc chloride (20 g.) was heated on the steam bath for 2 days. The white precipitate was filtered, washed with acetic acid and with methanol, and crystallized from N,N-dimethylformamide. The white needles (3.5 g. or 86%) melted at 251°–254° alone or in admixture with the compound obtained from *p*-chlorothiophenol (see Section (*a*)).

p-Chlorophenyl Ethyl Sulphide (*VII*)

This was prepared in quantitative yield by treating a hot alkaline solution of *p*-chlorothiophenol with diethyl sulphate in the usual manner. It boiled at 123° (18 mm.), n_D^{20} = 1.5800. Anal. Calc. for C_8H_9ClS: C, 55.67; H, 5.22. Found: C, 56.35; H, 5.72.

2-Ethylmercapto-5-chlorobenzyl Chloride (*VIII*)

A mixture of *p*-chlorophenyl ethyl sulphide (45 g.), acetic acid (200 ml.), paraformaldehyde (10 g.), and zinc chloride (10 g.) was saturated with hydrogen chloride and the resulting solution was heated on the steam bath for 20 hours. The reaction mixture was concentrated *in vacuo* to about one-half of its original volume and the residue treated with water and then extracted with benzene. The benzene extract was washed with water, with aqueous sodium bicarbonate, and with water, and the solvent removed. The residue was distilled yielding three fractions: fraction 1, b.p. (11 mm.) = 110°–135°, 4 g.; fraction 2, b.p. (11 mm.) = 135°–170°, 30 g.; and fraction 3, b.p. (11 mm.) = 200°–250°, 8 g. Fraction 2 was redistilled yielding a colorless liquid (20 g.) of VIII boiling at 150°–152° (11 mm.), n_D^{20} = 1.5933. Anal. Calc. for $C_9H_{10}Cl_2S$: C, 48.87; H, 4.52. Found: C, 49.23, 49.61; H, 4.41, 4.73.

Fraction 3 was crystallized from benzene yielding white prisms (0.7 g.) melting at 250°–252° alone or in admixture with *2,8-dichloro-6H,12H-dibenzo(b,f)-1,5-dithiocin* (*VI*) prepared from *p*-chlorothiophenol.

The mother liquors from the crystallization of fraction 3 were taken to dryness and the residue crystallized from methanol yielding white prisms (1 g.) melting at 96°–98° alone or in admixture with *2,2'-bis(ethylmercapto)-5,5'-dichlorodiphenylmethane* prepared from VII and VIII (see below).

2-Ethylmercapto-5-chlorobenzyl Isothiuronium Chloride

2-Ethylmercapto-5-chlorobenzyl chloride (16 g.), thiourea (5 g.), and ethanol (100 ml.) were heated together under reflux for 3 hours. The solvent was removed *in vacuo*, the residue was dissolved in warm water (300 ml.), the solution washed with benzene and then concentrated *in vacuo* to about 25 ml. The white needles (12 g.), which precipitated when the solution was cooled, were filtered, washed, and dried, m.p. 204°–206°. Anal. Calc. for $C_{10}H_{14}N_2Cl_2S_2$: C, 40.40; H, 4.71; N, 9.42. Found: C, 40.73, 40.73; H, 4.88, 4.85; N, 9.91, 9.99.

2,2'-Bis(ethylmercapto)-5,5'-dichlorodiphenylmethane (*IX*)

A reaction mixture of 2-ethylmercapto-5-chlorobenzyl chloride (VIII) (5 g.), *p*-chlorophenyl ethyl sulphide (VII) (5 g.), zinc chloride (12 g.), and acetic acid (25 ml.) was heated under reflux for 1 hour and then poured into dilute hydrochloric acid. The precipitated oil was extracted with benzene, the benzene solution was washed with water, and the solvent removed. The residue was distilled and the fraction boiling at 175°–190° (0.5 mm.) collected. When this distillate was crystallized twice from methanol it yielded white prisms (3.5 g.) melting at 95°–97°. Anal. Calc. for $C_{10}H_{14}N_2Cl_2S_2$: C, 57.13; H, 5.04. Found: C, 57.06, 57.31; H, 5.27, 5.17.

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STRUCTURE OF AN ARABOGALACTAN FROM WHITE SPRUCE (PICEA GLAUCA (MOENCH) VOSS)[1]

G. A. ADAMS

ABSTRACT

A water-soluble polysaccharide isolated from white spruce wood contained D-galactose, L-arabinose, and D-xylose in a molar ratio of 21:3:1. Hydrolysis of the fully methylated polysaccharide yielded 2,3,5-tri-*O*-methyl-L-arabinose (12 moles); 2,3,4,6-tetra-*O*-methyl-D-galactose (29 moles); 2,3,4-tri-*O*-methyl-D-galactose (34 moles); 2,6-di-*O*-methyl-D-galactose (0.5 moles); 2,4-di-*O*-methyl-D-galactose (45 moles); 2,3-di-*O*-methyl-D-xylose (5 moles); and monomethyl xylose (1 mole). When oxidized by periodate the polysaccharide consumed 1.18 moles of oxidant, and yielded 0.56 moles of formic acid per mole of anhydro-D-galactose. The D-xylose was attributed to the presence of a xylan mixed with the arabogalactan in the original polysaccharide preparation. The methylation and periodate oxidation data showed that the arabogalactan possessed a highly branched structure with the anhydro-D-galactose units being joined by 1→3 and 1→6 glycosidic bonds. All of the L-arabinose was present in the furanoside form as non-reducing terminal units.

Water-soluble polysaccharides of the arabogalactan type occur predominantly in the larches (1, 2, 3, 4, 5), although lesser amounts have been found in black spruce (*Picea mariana*) (6), southern yellow pine (*Pinus palustris*) (7), Jeffrey pine (*Pinus jeffreyi*) (8), and jack pine (*Pinus banksiana*) (9). The polysaccharides isolated from southern yellow pine and black spruce contained uronic acid residues in addition to arabinose and galactose. Fractionation of the water-soluble polysaccharides from the various sources has shown that some are heterogeneous. The heterogeneous nature of the polysaccharides from *Larix occidentalis* was demonstrated by Peterson *et al.* (10) and the arabogalactan from the European larch (*Larix decidua*) similarly was shown to be heterogeneous by Campbell *et al.* (11). On the other hand, the arabogalactans from Jeffrey pine (8) and jack pine (9) have been regarded as homogeneous. In an extensive investigation on the structure of the arabogalactan of western larch (*L. occidentalis*) (4, 12, 13, 14) White regarded the polysaccharide as homogeneous, a view which has been disputed by Campbell *et al.* (11).

A previous paper from this laboratory reported the isolation and composition of a

TABLE I

CHROMATOGRAPHIC SEPARATION OF METHYLATED SUGARS

Fractions from column	Methylated sugar	Yield (mg.)	$[\alpha]_D^{25}$ (water)
1 (Tube 45–88)	2,3,5-Tri-*O*-methyl-L-arabinose	242	−11°
2 (Tube 89–112)	2,3,4,6-Tetra-*O*-methyl-D-galactose	636	+94°
3 (Tube 113–138)	2,3,4,6-Tetra-*O*-methyl-D-galactose, dimethyl xylose	181	+73°
4 (Tube 139–200)	2,3,4-Tri-*O*-methyl-D-galactose	735	+104°
5 (Tube 201–214)	2,3,4-Tri-*O*-methyl-D-galactose, dimethyl galactose, monomethyl xylose	28	+70°
6 (Tube 215–218)	2,3,4-Tri-*O*-methyl-D-galactose, dimethyl galactose, monomethyl xylose	22	+64°
7 (Tube 219–234)	Impure 2,4-di-*O*-methyl-D-galactose	16	+68°
8 (Tube 235–305)	2,4-Di-*O*-methyl-D-galactose	893	+86°
9 (Tube 306–360)	Impure 2,4-di-*O*-methyl-D-galactose	83	+76°
10 (Tube 361–377)	Unknown	9	—
		2845 92% recovery	

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water-soluble polysaccharide from white spruce (*Picea glauca*) (15). It contained galactose, arabinose, xylose (molar ratio, 21:3:1), and a small amount of uronic acid (3.0%), and had a specific rotation $[\alpha]_D^{25} = -7°$. Results of several fractionation procedures indicated that the polysaccharide was essentially homogeneous and this conclusion was further confirmed by electrophoretic examination.

The present investigation was concerned with the structure of the polysaccharide as shown by methylation and periodate oxidation studies. The polysaccharide was methylated and the methyl ether subjected to methanolysis and hydrolysis. The methylated sugars were separated chromatographically on a Celite column (16) into 10 fractions as shown in Table I.

Further separations of mixtures were made and the main methylated sugars were characterized by isolation of appropriate crystalline derivatives. The amounts and molar ratios of the various sugar components are shown in the following table.

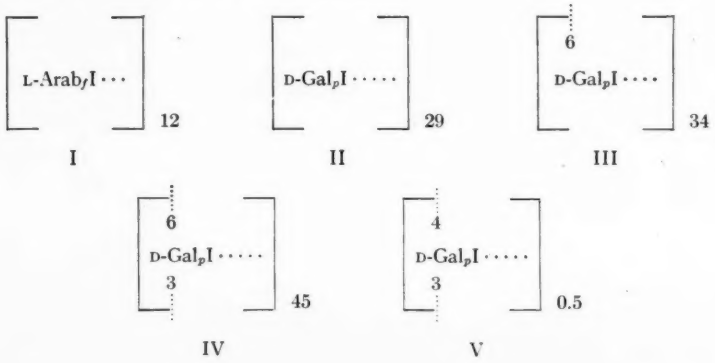
TABLE II

YIELD OF METHYLATED SUGARS

Methylated sugar	Wt. (mg.)	Millimoles	Molar ratio
2,3,5-Tri-*O*-methyl-L-arabinose	236	1.23	12
2,3,4,6-Tetra-*O*-methyl-D-galactose	695	2.94	29
2,3,4-Tri-*O*-methyl-D-galactose	758	3.43	34
2,6-Di-*O*-methyl-D-galactose	10	0.05	0.5
2,4-Di-*O*-methyl-D-galactose	942	4.55	45
2,3-Di-*O*-methyl-D-xylose	89	0.50	5
Monomethyl xylose	18	0.10	1

The polysaccharide was considered to be an arabogalactan and the small amount of xylose present after hydrolysis was attributed to an admixed xylan. The methylation data showed that the xylan had the usual 1→4 linked structure with some branching present at $C_{(2)}$ and/or $C_{(3)}$. No tri-*O*-methyl-D-xylose, representative of the non-reducing end of the xylan, could be found, undoubtedly because the amount present was too small to be detected. The presence of xylan of the usual type which has a characteristically high negative rotation could account for the present polysaccharide having a slightly negative specific rotation (−7°) compared with the small positive rotation previously reported for arabogalactans (10, 8, 9).

Results of the methylation studies showed that the arabogalactan must contain the following units, in the relative amounts shown:



The high proportion of terminal units of arabinose (I) and galactose (II) showed that the polysaccharide molecule was highly branched, the branches occurring at positions as shown by III, IV, and V. Although the present data do not permit the assignment of a unique structure to the molecule, certain structural features are evident. The main chain or "backbone" of the molecule can be visualized as D-galactopyranose units linked 1→6. The relatively high proportion of IV showed that considerable branching occurred at $C_{(3)}$ and subsidiary chains of 1→6 linked D-galactopyranose units could be attached at this point. This arrangement provides for a branch-on-branch type of structure terminated at the non-reducing ends by unsubstituted D-galactopyranose and L-arabofuranose residues. The small amount of 2,6-di-*O*-methyl-D-galactose (0.5 moles) found in the hydrolysis products showed that a small amount of branching also occurred at $C_{(3)}$ and $C_{(4)}$ of some anhydro-D-galactose units. The number of sugar units (45.5) forming branch points (IV and V) was slightly more than the number (41) of non-reducing terminal units (I and II). The ratio of methylated arabinose to methylated galactose (12:108) found on hydrolysis was less than that in the original polysaccharide molecule (arabinose: galactose 1:7). Both of these discrepancies were probably caused by some loss of the volatile methyl glycoside of 2,3,5-tri-*O*-methyl-L-arabinose. No partially methylated arabinose units were present after hydrolysis and hence the likelihood was remote that the 2,3,5-tri-*O*-methyl-L-arabinose had its origin in an admixed araban. The absence of unoxidized arabinose units after treatment with periodate further confirmed these conclusions. The change in specific rotation on hydrolysis of the methylated polysaccharide ($[\alpha]_D^{25}$ −55 to +75°) indicated that the glycosidic bonds were mainly in the β-configuration. An arabogalactan having structural features as described should consume 1.15 moles of periodate per mole of anhydro-D-galactose and produce 0.55 moles of formic acid; the actual values of 1.18 moles of periodate and 0.56 moles of formic acid provided excellent agreement.

The structural features of the white spruce arabogalactan conform in general to those found in other arabogalactans of wood (12, 13, 14, 8, 9, 11). These structural characteristics include a high degree of branching through positions 6 and 3 of the anhydro-D-galactose units with the arabinose units attached as end groups on some of the branches. The white spruce arabogalactan resembled rather closely the arabogalactan of jack pine (9) although the latter contained proportionately less arabinose. It differed from the arabogalactan of Jeffrey pine (8) by having its arabinose units exclusively in terminal positions and also a greater proportion of the galactose units as non-reducing end groups. The arabogalactan of larch (14) differed by having more branching at position 3 of the galactose units.

The problem of heterogeneity makes positive interpretation of the methylation and periodate oxidation data difficult; the existence of a galactan admixed with the arabogalactan is a possibility that cannot be excluded.

EXPERIMENTAL

All specific rotations are equilibrium values unless otherwise stated and melting points are corrected.

Paper Chromatography

Chromatographic separations were carried out using the following solvent systems (v/v ratios): (A) pyridine:ethyl acetate:water (2:1:2); (B) methyl ethyl ketone:water (2:1); (C) ethanol:benzene:water (47:200:15); (D) *n*-butanol: ethanol:water (40:11:19); and (E) ethyl acetate:acetic acid:formic acid:water (18:3:1:4). Separations were per-

formed by the descending technique on Whatman No. 1 filter paper. Methylated sugars were located on the papers by *p*-anisidine hydrochloride spray reagent (17).

Composition of the Polysaccharide

The polysaccharide was prepared from a water-soluble extract of white spruce (*Picea glauca* (Moench) Voss) as described previously (15). The material was soluble in water and had the following analysis: D-galactose, L-arabinose, and D-xylose (molar ratio 21:3:1); Klason lignin, 3.0%; ash (sulphated), 2.5%; uronic acid 3.3% and $[\alpha]_D^{25} = -7° \pm 2.5°$ (*c*, 0.7% in 10% sodium hydroxide).

Methylation

Hemicellulose (6.40 g.) was dissolved in water (25 ml.) and methylated by the dropwise addition of dimethyl sulphate (60 ml.) and 45% sodium hydroxide solution (100 ml.) with stirring. The reagent additions required a period of 4 hours and the solution was kept alkaline at all times. After stirring for 1 hour, the foregoing methylation was repeated and the solution was stirred overnight. Complete methyl glycoside formation was indicated by a negative reduction test with Fehling's solution. A 100-ml. quantity of 45% sodium hydroxide was added at one time and further methylation carried out by the addition of dimethyl sulphate (60 ml.) over 3 hours. This treatment was repeated once more, the reaction mixture being stirred overnight and then heated at 85° C. for $1\frac{1}{2}$ hours. The solution was cooled in an ice bath and brought to pH 7.0 with acetic acid. The salts were dissolved by the addition of water and the partially methylated polysaccharide was extracted by shaking with chloroform. The extracts were dried by anhydrous sodium sulphate and evaporated to yield a glassy solid (4.10 g.). Dialysis of the extracted water phase, followed by freeze-drying of the salt-free solution, yielded a further quantity of partially methylated polysaccharide (1.74 g.). Three additional methylations of this fraction, as described above, followed by chloroform extraction, yielded a more highly methylated polysaccharide (1.04 g.). Both fractions showed a definite hydroxyl band at 3500–3600 cm.$^{-1}$ in their infrared spectra. The fractions were combined (wt. = 5.14 g.) and dissolved in tetrahydrofurane (100 ml.). Powdered sodium hydroxide (35 g.) and dimethyl sulphate (35 ml.) were added, the latter over a period of 4 hours. Recovery of the methylated polysaccharide by chloroform extraction as described before yielded a glassy solid (3.69 g.) which still showed a distinct hydroxyl band in its infrared spectrum. The partially methylated product was dissolved in methyl iodide:methanol (100:5) and methylated by addition of silver oxide (10 g.) in portions of 2 g. every hour. The solution was refluxed overnight and the methylated product was recovered by extraction with chloroform. Three additional methylations by this method were necessary to yield a product which had no hydroxyl band at 3500–3600 cm.$^{-1}$ in its infrared spectrum. The methylated polysaccharide was a yellowish solid (3.96 g.) having $[\alpha]_D^{25} = -55° \pm 1°$ (*c*, 1.0% in chloroform) and OMe 42.8% (theoretical value for $(C_9H_{16}O_5)_n$, 45.3%).

Hydrolysis of Methylated Polysaccharide

The methylated polysaccharide (3.96 g.) was heated with 8% methanolic hydrogen chloride (150 ml.) in a boiling water bath for 12 hours. Methanol was evaporated by a stream of air from a fan at room temperature, *N* hydrochloric acid (60 ml.) was added, and the methyl glycosides were hydrolyzed on a boiling water bath for 10 hours. A small insoluble precipitate was filtered off and the acidic solution was neutralized by Amberlite 1R-45 resin. The neutral solution was concentrated to a thin sirup, taken up in aqueous ethanol, clarified with charcoal, and concentrated to a thick sirup. After

further drying over calcium chloride in a desiccator *in vacuo* the product weighed 3.18 g. and had $[\alpha]_D^{25} = +75° \pm 1°$ (*c*, 1.56 in water). Chromatographic examination of the sirup on paper strips (solvent D) indicated the presence of the following methylated sugars: 2,3,5-tri-*O*-methyl-L-arabinose (R_g 0.96); 2,3,4,6-tetra-*O*-methyl-D-galactose (R_g 0.92); 2,3,4-tri-*O*-methyl-D-galactose (R_g 0.76); 2,4-di-*O*-methyl-D-galactose (R_g 0.54); 2,6-di-*O*-methyl-D-galactose (R_g 0.58); 2,3-di-*O*-methyl-D-xylose (R_f 0.50–0.52, solvent B); and a methylated uronic acid.

Separation of Methylated Sugars

The mixture of methylated sugars (3.1 g.) was separated on a Celite column using *n*-butanol saturated with water as the developing phase (16). The eluate was collected by an automatic fraction collector in 15 ml. quantities at 2½-minute intervals. Chromatographic examination of every fifth tube on paper strips (solvent D) permitted the grouping of fractions of similar composition. The fractions were taken to dryness and weighed; Table I gives yields and the rotations of the various fractions without further purification. A small amount of uronic acid was removed from the column with water. As the amount was small and the acid was mixed with partially methylated sugars it was not examined further.

Identification of the Methylated Sugars

Fraction 1.—The sugar was dissolved in water, charcoal was added, the solution filtered and taken to dryness (236 mg.). Chromatographic examination in solvents B, C, and D showed that this sugar moved at the same rate as 2,3,5-tri-*O*-methyl-L-arabinose. Specific rotation $[\alpha]_D^{25} = -35° \pm 1°$ and OMe, 47.6% (calculated for $C_8H_{16}O_5$: OMe, 48.4%) further identified it as 2,3,5-tri-*O*-methyl-L-arabinose. The amide of the corresponding arabonic acid was prepared as follows: a portion of the sirup (140 mg.) was dissolved in water (3 ml.) and oxidized by bromine (0.5 ml.) for 50 hours at room temperature. After removal of the bromine by aeration, the solution was neutralized with silver carbonate; excess silver ions were removed by hydrogen sulphide. The solution was evaporated to dryness and 2,3,5-tri-*O*-methyl-L-arabonic acid recovered as a sirup. The acid was lactonized by distillation (bath temperature 120°–145° C. at 0.025 mm.). Addition of methanol saturated with ammonia to the lactone for 24 hours at 5° C. yielded the amide which was recovered by removal of the solvent in a desiccator. The amide crystallized on nucleation and on recrystallization from methanol–ether solution yielded pure 2,3,5-tri-*O*-methyl-L-arabonamide, m.p. 136° (undepressed with an authentic sample) and $[\alpha]_D^{25} = -18° \pm 3°$ (*c*, 1% in water); these values agree with those reported for this compound (18).

Fraction 2.—This sugar (636 mg.) was identical with 2,3,4,6-tetra-*O*-methyl-D-galactose when compared chromatographically in solvents B, C, and D. A portion of the sirup (96.4 mg.) was refluxed with aniline (50 mg.) in ethanol (5 ml.) for 2½ hours. The aniline derivative crystallized during the heating period and after recrystallization from ethanol had a m.p. and mixed m.p. 196°–197° C. and $[\alpha]_D^{25} = -137° \pm 1°$ (*c*, 0.92 in pyridine) and thus was identified as 2,3,4,6-tetra-*O*-methyl-N-phenyl-D-galactosylamine (19).

Fraction 3.—Chromatographic evidence indicated that this sirup (181 mg.) was a mixture of 2,3,4,6-tetra-*O*-methyl-D-galactose and a dimethyl xylose. Separation was achieved on an alumina column (15 × 80 mm.) using the solvents listed below and the eluates were collected on an automatic fraction collector. The presence of the various sugars was indicated by spotting 10 drops of the eluate on paper and spraying with *p*-anisidine reagent. The results are as follows:

Fraction	Solvent	Compound	Yield (mg.)
3A (Tube 9–47)	Chloroform	2,3,4,6-Tetra-*O*-methyl-D-galactose	59
3B (Tube 48–78)	Ethanol	Dimethyl xylose	57
3C (Tube 79–100)	Water	Dimethyl xylose	32

Subfraction 3A.—This sirup was chromatographically identical in solvents B, C, and D with 2,3,4,6-tetra-*O*-methyl-D-galactose. The sirup (52 mg.) was converted as described above into its aniline derivative which had a m.p. of 196° C. and $[\alpha]_D^{25} = -137° \pm 1°$ (*c*, 1.0% in pyridine).

Subfraction 3B.—This sirup (57 mg.) travelled at the same rate on a paper chromatogram as 2,3-di-*O*-methyl-D-xylose in solvents B, C, and D. These solvents served to distinguish it from 2,4-di-*O*-methyl-D-xylose and also 3,4-di-*O*-methyl-D-xylose (20). A portion of the sugar (46 mg.) was heated with aniline (28.6 mg.) in ethanol (5 ml.) for 3 hours. Slow removal of the solvent in a desiccator containing calcium chloride under reduced pressure yielded crystals of 2,3-di-*O*-methyl-N-phenyl-D-xylosylamine, which on recrystallization from ethyl acetate solution had a m.p. and mixed m.p. of 126° C., reported value 126° C. (21).

Subfraction 3C.—This fraction (32 mg.) was found to be 2,3-di-*O*-methyl-D-xylose by the chromatographic separations applied to subfraction 3B.

Fraction 4.—The sirup (735 mg.) was chromatographically identical in solvents B and D with 2,3,4-tri-*O*-methyl-D-galactose. The identity of the sugar was established by formation of the amide of the corresponding galactonic acid as follows: a portion of the sirup (133.2 mg.) was dissolved in water (2 ml.) and bromine (0.5 ml.) was added and the oxidation was allowed to proceed for 50 hours. Bromine was removed by aeration and the acidity was neutralized with silver carbonate. The 2,3,4-tri-*O*-methyl-D-galactonic acid was lactonized by distillation (bath temperature 150°–170° C./0.02 mm.). Addition of methanolic ammonia yielded 2,3,4-tri-*O*-methyl-D-galactonamide, m.p. and mixed m.p. 166°–167° C. and $[\alpha]_D^{25} = 32.5° \pm 2°$ (*c*, 1% in water) in good agreement with the reported value (22). Further confirmation of identity was provided by preparation of the corresponding anilide by refluxing the sugar (86.4 mg.) with aniline (44.6 mg.) in ethanol (5 ml.) for 3 hours. Removal of solvent yielded crystals which on recrystallization from ethyl acetate proved to be 2,3,4-tri-*O*-methyl-N-phenyl-D-galactosylamine, m.p. and mixed m.p. 165°–166° C. and $[\alpha]_D^{25} = 40° \pm 2°$ (*c*, 1.2% in methanol); melting points of 164° C. and 167° C. have been reported (19, 22).

Fraction 5.—Chromatographic examination in solvents B and D showed that this sirup (28 mg.) was a mixture of a trimethyl galactose, dimethyl galactose, and a monomethyl xylose. The rate of movement in solvent D showed that the trimethyl galactose (R_g 0.73–0.75) was identical with 2,3,4-tri-*O*-methyl-D-galactose, the dimethyl-D-galactose (R_g 0.59–0.60) was identical with 2,6-di-*O*-methyl-D-galactose and different from 2,4-di-*O*-methyl-D-galactose (R_g 0.51–0.52). The monomethyl xylose was chromatographically indistinguishable in solvents B and D from 2-*O*-methyl-D-xylose and 3-*O*-methyl-D-xylose. The ratio of the three sugars in the mixture was determined, after spraying with *p*-anisidine reagent, by modifying a densitometer method described for unsubstituted sugars (23); the ratio found for the three methylated sugars was 4:1:1.

Fraction 6.—This sirup (22 mg.) was also a mixture as shown by chromatographic examination in solvents B and D and contained the same sugars as Fraction 5. The component sugars 2,3,4-tri-*O*-methyl-D-galactose, 2,6-di-*O*-methyl-D-galactose, and monomethyl xylose were present in a ratio of approximately 1:1:2.

Fraction 7.—The sirup (16 mg.) was chromatographically identical in solvents B and D with 2,4-di-*O*-methyl-D-galactose and had $[\alpha]_D^{25} = +83° \pm 1°$ constant value in 24 hours (*c*, 1% in water). This material was identical with the main Fraction 8 and no further identifications were made.

Fraction 8.—The sirup (893 mg.) crystallized when it was left standing and it corresponded chromatographically in solvents B and D to 2,4-di-*O*-methyl-D-galactose. On recrystallization from ether, 2,4-di-*O*-methyl-D-galactose monohydrate (22) was obtained, m.p. 100°–101° C. with sintering at 73°–76° C., $[\alpha]_D^{25} = +125°$ (5 minutes) $\rightarrow +84° \pm 1°$ in 24 hours (*c*, 1% in water). Anhydrous 2,4-di-*O*-methyl-D-galactose was obtained by drying the monohydrate at 55° C. at 0.1 mm. over phosphorus pentoxide for 20 hours. The anhydrous product had a m.p. and mixed m.p. 103°–104° C. (no sintering) and $[\alpha]_D^{25} = 125°$ (5 minutes) $\rightarrow +87° \pm 1°$ in 24 hours (*c*, 1% in water) in good agreement with the reported values (9). A portion of the sugar (77.0 mg.) was refluxed with aniline (40.2 mg.) in ethanol (5 ml.) for 3 hours. The aniline derivative was obtained in crystalline form on evaporation of the reaction mixture and on recrystallization from ethyl acetate yielded 2,4-di-*O*-methyl-N-phenyl-D-galactosylamine (22) having a m.p. and mixed m.p. 218°–220° C. and $[\alpha]_D^{25} = -181° \pm 4°$ (*c*, 0.92 in pyridine).

Fraction 9.—The sirup (83 mg.) partially crystallized when it was left standing and was chromatographically identical in solvents B and D with 2,4-di-*O*-methyl-D-galactose. Recrystallization from ether yielded 2,4-di-*O*-methyl-D-galactose monohydrate (40 mg.), m.p. and mixed m.p. 100°–101° C. with sintering at 73°–76° C. and $[\alpha]_D^{25} = +125°$ (5 minutes) $\rightarrow +84° \pm 1°$ in 24 hours (*c*, 1.2% in water).

Fraction 10.—The sirup (9 mg.) on chromatographic examination in solvents B and C appeared to be a monomethyl galactose. The material was not investigated further.

The amounts of the main methylated sugar components and their molar ratios are given in Table II.

Periodate Oxidation

Spruce polysaccharide (100 mg. duplicate samples) was dissolved in water (50 ml.) and oxidized by 0.1 *M* sodium periodate (50 ml.) in the dark at 16° C. Analysis for periodate consumption and formic acid production (24) gave the following results:

Time, hours	12	22	72	120	144
Formic acid, moles per $C_5H_8O_4$	0.51	0.55	0.65	0.71	0.73
Periodate consumption, moles per $C_5H_8O_4$	1.03	1.12	1.29	1.37	1.40

The time at which the oxidation was completed was found by extrapolating the flat portion of the time curve to zero time. The values of 1.15 moles of periodate per mole of anhydrogalactose residue and 0.55 moles of formic acid were obtained. In a separate experiment, 50 mg. of the polysaccharide was oxidized for 48 hours, the excess periodate was destroyed by the addition of 2,3-butanediol and the solution dialyzed. The nondialyzable solids were recovered by freeze-drying and then hydrolyzed with *N* sulphuric acid. Chromatographic examination of the neutralized solution showed galactose to be the only sugar present.

ACKNOWLEDGMENTS

The author wishes to thank A. E. Castagne for valuable technical assistance throughout the course of this investigation. Thanks are also tendered to Dr. H. Schwartz, Superintendent, Forest Product Laboratories, Ottawa, Canada, who kindly supplied an authenticated specimen of white spruce wood.

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STUDIES IN THE WAGNER–MEERWEIN REARRANGEMENT. PART III[1]

F. A. L. ANET AND P. M. G. BAVIN[2]

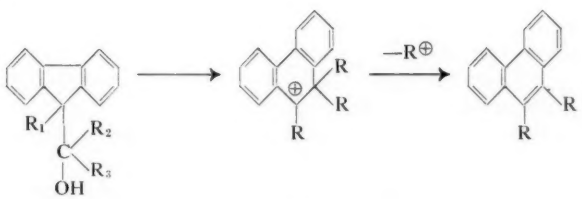
ABSTRACT

2-(9-Methyl-9-fluorenyl)-propan-2-ol and 3-(9-ethyl-9-fluorenyl)-pentan-3-ol have been prepared and shown to give 9,10-dimethyl- and 9-10-diethylphenanthrene, respectively, when heated with polyphosphoric acid.

In Part I of this series (1), we reported that dehydration-rearrangement of 9-*t*-butyl-9-fluorenylmethanol (I, R_1 = *t*-butyl; R_2 = R_3 = hydrogen) by the action of polyphosphoric acid gave rise to a considerable amount of phenanthrene. Since 9-*t*-butylphenanthrene was stable under these conditions, loss of the alkyl group appeared to take place during the rearrangement process. Accordingly, we tried to prepare 2-(9-*t*-butyl-9-fluorenyl)-propan-2-ol (I, R_1 = *t*-butyl; R_2 = R_3 = methyl), which was expected to lead to 9,10-dimethylphenanthrene by expulsion of the *t*-butyl group and a double Wagner–Meerwein rearrangement. Our attempts to prepare this carbinol from methyl 9-*t*-butylfluorene-9-carboxylate have failed (see below), but we have made some related carbinols in which rearrangement and aromatization involved expulsion of an alkyl group.

Methyl magnesium iodide reacted with methyl 9-methylfluorene-9-carboxylate to give 2-(9-methyl-9-fluorenyl)-propan-2-ol (I, R = methyl) in 70–80% yield. Heating of this alcohol with polyphosphoric acid gave 9,10-dimethylphenanthrene. Similarly, ethyl magnesium iodide reacted with methyl 9-ethylfluorene-9-carboxylate to give 3-(9-ethyl-9-fluorenyl)-pentan-3-ol (I, R = ethyl), which gave by heating with polyphosphoric acid 9,10-diethylphenanthrene. In both reactions with polyphosphoric acid the yield of crude hydrocarbon was about 30–50%, but only about 4–10% was obtained completely pure.

These rearrangements may be represented as shown below. It is possible that a shuffling of the alkyl groups in II takes place, and this point could be examined by using suitably labelled alkyl groups.



I II

The increase in resonance energy on passing from II to the 9,10-dialkylphenanthrene probably supplies the driving force for the expulsion of the alkyl group (R).

It was shown previously (1) that methyl 9-*t*-butylfluorene-9-carboxylate was saponified much more slowly than the 9-methyl compound, the difference being attributed to steric hindrance in the former compound. In agreement with this we have found that the 9-*t*-

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Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada.
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butyl derivative was recovered unchanged after boiling for 1 hour with ethereal methyl magnesium iodide. Prolonged reaction with lithium methyl or the Grignard reagent gave a mixture which we were unable to resolve.

EXPERIMENTAL

Preparation of the Tertiary Carbinols

Methyl 9-methylfluorene-9-carboxylate (1) (3 g.) was boiled under reflux for 2 hours with ethereal methyl magnesium iodide (6 equivalents). The complex was decomposed with ice and ammonium chloride. Evaporation of chloroform extracts gave an oil which crystallized when left overnight in the ice chest under a little hexane. Recrystallization from hexane gave *2-(9-methyl-9-fluorenyl)-propan-2-ol* as long, colorless prismatic needles (2.1 g., 70%), m.p. 68°–69°. Found: C, 85.75; H, 7.52%. Calc. for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

Reaction of methyl 9-ethylfluorene-9-carboxylate (1) with ethyl magnesium iodide gave, in the same way, *3-(9-ethyl-9-fluorenyl)-pentan-3-ol* in 79% yield. It crystallized from hexane as short stout prisms, m.p. 103°–105°. Found: C, 85.55; H, 8.40%. Calc. for $C_{20}H_{24}O$: C, 85.66; H, 8.63%.

The infrared spectra of carbon disulphide solutions of the carbinols showed strong O–H stretching bands at 3615 $cm.^{-1}$. Solutions of the carbinols in cold concentrated sulphuric acid were carmine.

The crude carbinols melted over a wide range and 20°–30° below the pure compounds, although the infrared spectra did not show carbonyl absorption. It is likely that the carbinols have high molar depression constants, as have been found for other highly branched compounds (2).

Reaction of the Carbinols with Polyphosphoric Acid

The methyl carbinol (1 g.) and polyphosphoric acid (150 ml.) were heated together with stirring at 160° for 1 hour and then at 180° for 15 minutes. The cooled mixture was poured onto ice and extracted with chloroform. Evaporation left an oil which was dissolved in hexane and purified by passage through a column of alumina. Further elution and subsequent evaporation gave a colorless oil. Crystallization from methanol–acetone gave white needles, m.p. 134°–137°, raised to 142°–144° by three more crystallizations. The melting point was not depressed when the compound was mixed with authentic 9,10-dimethylphenanthrene (3), m.p. 143°–144°. Alternatively the hydrocarbon was purified through its picrate or trinitrobenzene complex.

In a similar way the ethyl carbinol gave 9,10-diethylphenanthrene, which formed glistening plates, m.p. 103°–105°, after four crystallizations from methanol–acetone. The melting point was not depressed when the compound was mixed with authentic 9,10-diethylphenanthrene (4), m.p. 106°–107°. The identities were confirmed by comparison of infrared spectra.

Attempted Preparation of 2-(9-t-Butyl-9-fluorenyl)-propan-2-ol

Methyl 9-*t*-butylfluorene-9-carboxylate (1) (12 g.) and ethereal methyl magnesium iodide (12 equivalents) were boiled under reflux for 24 hours. The product was isolated in the usual way, dissolved in hexane, and passed through a short column of activated alumina. When the product was concentrated to 15 ml. and left standing in the ice chest for 3 weeks it gave colorless prisms (7.4 g.). These were collected, washed with a little ice-cold pentane, and recrystallized from hexane (10 ml.) as before to give 4.2 g. of prisms, m.p. 70°–71°. The infrared spectrum of a chloroform solution did not show

hydroxyl or carbonyl absorption. The yield of this compound was erratic. A solution of the crude product in carbon bisulphide showed an O–H stretching band at 3618 cm.$^{-1}$.

ACKNOWLEDGMENT

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SOME STRUCTURAL FEATURES OF DELCOSINE[1]

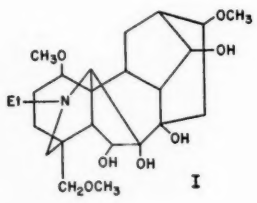
RAGINI ANET[2] AND LÉO MARION

ABSTRACT

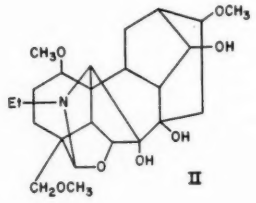
The alkaloid delcosine has previously been assigned tentatively the same carbon–nitrogen skeleton as lycoctonine to which it appears to be closely related in properties. Oxidation experiments now reported provide supporting evidence of the presence of two vicinal tertiary hydroxyl groups attached to a five- and a six-membered ring that are directly linked together at the two carbons carrying the hydroxyls. There is a methoxyl in a position β to the tertiary hydroxyl of the six-membered ring. Evidence is also provided as to the size of the heterocyclic ring and the presence of a methylene group next to the nitrogen.

The tentative structure I previously advanced for delcosine ($C_{24}H_{39}O_7N$) was based on an assumed relationship with the alkaloid lycoctonine, and on the possibility on this assumption[3] of explaining the nature of the oxidation products that had been described (1). We now wish to report further oxidation studies carried out with anhydrohydroxydelcosine II ($C_{24}H_{37}O_7N$), which lend support to some of the features of structure I.

Whereas lycoctonine (2) and demethylenedelpheline (3) yield oxo-derivatives that can be cleaved smoothly with periodic acid or lead tetraacetate, the corresponding bases are not oxidized in a satisfactory manner under the same conditions. Similarly, treatment of delcosine with periodic acid or sodium periodate at room temperature resulted in 4.5 moles of the reagent being consumed in 120 hours, the oxidation continuing until 21 moles had been consumed. The behavior with lead tetraacetate was equally indefinite.[4]



I



II

Anhydrohydroxydelcosine, an oxidation product which has been formulated as II, is much less basic than delcosine (1) and thus was expected to lend itself to cleavage with periodic acid more satisfactorily than the alkaloid. Indeed, it has now been found that on treatment with periodic acid at room temperature, anhydrohydroxydelcosine consumes 1 mole of the reagent in 24 hours. It has not been possible to obtain the oxidation product crystalline even after purification by chromatography on alumina, but its infrared absorption spectrum (in chloroform) contained two carbonyl bands at 1750 and 1710 cm.$^{-1}$ (no aldehyde stretching band at 2600–2800 cm.$^{-1}$) characteristic of a five- and a six-membered ketone respectively, as well as a band at 1000 cm.$^{-1}$ shown also by the spectrum of anhydrohydroxydelcosine in the same solvent. Clearly the oxidation product

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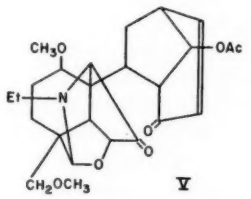
Issued as N.R.C. No. 4678.
[2]*National Research Council of Canada Postdoctorate Fellow.*
[3]*In the paper cited as Ref. (1), formula VII is an error. It should have been the formula of lycoctonine corresponding to the diterpenoid representation VIII. As given, VII is the formula of delcosine, and corresponds to the diterpenoid representation IX.*
[4]*These titration experiments were performed by Dr. D. W. Clayton.*

is anhydrohydroxydelcosine-*seco*diketone III formed by cleavage of a vicinal glycol system in which one of the hydroxyls is a substituent on a five-membered ring, and the other on a six-membered ring.

Although the *seco*diketone III could not be induced to crystallize, it formed a crystalline acetyl derivative IV ($C_{26}H_{37}O_8N$). In the infrared this derivative showed bands at 1763 and 1705 cm.$^{-1}$ characteristic of the carbonyls of a five-membered and a six-membered cyclic ketone, and at 1738 and 1233 cm.$^{-1}$ due to the acetate grouping. There was no absorption in the hydroxyl region. On treatment with acid under carefully controlled conditions, the acetyl derivative IV lost the elements of methanol and gave rise to desmethanol-anhydrohydroxydelcosine-*seco*diketone acetate, $C_{25}H_{33}O_7N$ (V), which in the infrared showed absorption bands at 1760, 1740, 1680, and 1615 cm.$^{-1}$. The shift in the frequency of the carbonyl band of the six-membered cyclic ketone from 1705 to 1680 cm.$^{-1}$ corresponds to the change to be expected in going from a saturated to an α,β-unsaturated ketone (4). In the ultraviolet spectrum of V the absorption at λ_{max} 232 mμ, logϵ 3.89, was somewhat higher than expected for an α,β-unsaturated-β-monosubstituted ketone (5) although the same as that occurring in the spectrum of desmethanol-hydroxylycoctonam-*seco*diketone (λ_{max} 230–233 mμ, logϵ 3.74) (6). Hence it is very probable that the double bond in V is α,β- to the carbonyl of the six-membered cyclic ketone. This parallels the chemistry of lycoctonine, and provides evidence concerning the vicinal glycol in delcosine and its environment. Consequently, on the basis of the proposed structure I, the desmethanol-derivative V can be represented as follows:



V

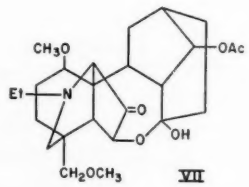
The amorphous anhydrohydroxydelcosine-*seco*diketone III was reduced with sodium borohydride to a compound VI ($C_{23}H_{37}O_6N$) which had lost the elements of methanol. Under the alkaline conditions of the reduction, the β-methoxyl group had been eliminated, and the carbonyls of both the six-membered and five-membered cyclic ketones had been reduced to secondary alcoholic groups. The infrared spectrum of VI showed no absorption in the carbonyl region. The presence of a double bond was confirmed by catalytic hydrogenation in the course of which 1 mole of hydrogen was absorbed smoothly. The behavior of the derivative III, on reduction, was markedly different from that of lycoctonam-*seco*diketone in which only the five-membered, but not the six-membered, ketone was reduced (2). A plausible explanation for this difference is that the internal ether present in compound V orients the carbonyls away from each other so that neither is hindered.

Hydrogenation of the *seco*diketone acetate IV, or its desmethanol-derivative V, in the presence of Adams' catalyst gave erratic results, but in the presence of palladium–charcoal in 50% acetic acid the compound V absorbed 2 moles of hydrogen in 30 minutes. No further absorption took place in the next 2 hours. The product was a crystalline compound VII ($C_{25}H_{37}O_7N$) obtained in 90% yield. Since under similar conditions anhydrohydroxydelcosine was rapidly reduced to delcosine (1), it was assumed that in the product VII the internal ether as well as the double bond had been hydrogenated. The

infrared absorption spectrum of VII contained bands at 3475 cm.$^{-1}$ indicative of a hydroxyl group; and at 1743, 1728, and 1255 cm.$^{-1}$, the first attributable to a five-membered ketone and the last two to an acetate group. The fact that no absorption occurred at 1700–1720 cm.$^{-1}$ whereas a well-resolved band in that region was present in the spectrum of the *seco*diketone acetate IV seemed to indicate that the six-membered ketone was no longer present in VII. Of the two moles of hydrogen absorbed, one was taken up by the double bond, the other must have reduced the internal ether, and therefore, the disappearance of the carbonyl of the six-membered ketone must be attributed to a rearrangement.

The reduction product VII, when oxidized with potassium permanganate in acetone containing acetic acid, gave rise to a neutral product VIII ($C_{25}H_{35}O_8N$). This neutral product had an infrared absorption spectrum containing bands in the hydroxyl region at 3470 cm.$^{-1}$ and in the carbonyl region at 1762 cm.$^{-1}$ characteristic of a five-membered cyclic ketone, at 1728 and 1255 cm.$^{-1}$ due to an acetate group, and at 1665 cm.$^{-1}$ indicative of an amide carbonyl. On vigorous alkaline hydrolysis, compound VIII produced a gum that could not be crystallized, but still showed in the infrared an absorption band at 1640 cm.$^{-1}$ (in chloroform). It has been shown previously that N-acetyl-N-desethyldelcosine is deacetylated readily under milder conditions, and hence it can be concluded that compound VIII does not contain an aliphatic amide but a lactam which from the frequency of its absorption in the infrared must be at least six-membered. This is the first evidence of the size of the heterocyclic ring in delcosine and of the presence next to the nitrogen of a methylene group consistent with the tentative structure I.

Delcosine is readily oxidized to a carbinolamine internal ether, anhydrohydroxydeclosine II, formed by elimination of water between the carbinolamine hydroxyl and one of the hydroxyls originally present in the base (1). Hence, to account for the facile oxidation of the compound VII to a lactam, it seems necessary to assume that in the course of the hydrogenation in which compound VII was produced, the hydroxyl liberated from the internal ether by reduction must have become masked. A possible explanation is that in the conversion of V to VII, this hydroxyl, set free by the hydrogenation, forms a hemiketal with the carbonyl of the six-membered ketone so that VII could be represented as follows:



VII

The oxidation product VIII would therefore be the corresponding lactam. The infrared spectra of both VII and VIII seem to be in agreement with the presence of a hemiketal, since they contain absorption bands in the regions 1158–1190, 1124–1143, and 1063–1098 cm.$^{-1}$ (cf. 7).

EXPERIMENTAL

Ultraviolet absorption spectra were recorded with a Beckman DU spectrophotometer. The infrared absorption spectra were recorded with a Perkin-Elmer double-beam model

21 instrument with a rock salt prism. Unless otherwise mentioned the samples were suspended in nujol. All melting points were determined on a microscope hot stage and are uncorrected.

Cleavage of Anhydrohydroxydelcosine with Periodic Acid

To anhydrohydroxydelcosine (146 mg.) in water (5 ml.) 0.12 *M* periodic acid (1.5 ml.) was added and the mixture kept at room temperature in the dark for 25 hours. The aqueous solution was neutralized with sodium bicarbonate and extracted with chloroform. On evaporation, the extract yielded a gum which was dissolved in benzene and chromatographed on neutral alumina (activity III). Anhydrohydroxydelcosine-*seco*diketone was eluted from the column with benzene–ether (1:1). It consisted of a gum that could not be crystallized but was converted to an amorphous white solid in contact with petroleum ether. Its infrared absorption spectrum contained carbonyl bands at 1755 and 1710 $cm.^{-1}$.

O-Acetyl-anhydrohydroxydelcosine-secodiketone

Anhydrohydroxydelcosine (164 mg.) in periodic acid (3 ml.) was allowed to stand for 27 hours. The crude product, obtained as described above, was added to acetic anhydride (5 ml.) containing a few drops of pyridine, and left at room temperature for 18 hours. The acetic anhydride and pyridine were distilled off under reduced pressure at a temperature not exceeding 60°. The residue was dissolved in chloroform and the solution washed with dilute sodium bicarbonate and with water. The combined aqueous washings were extracted with a fresh quantity of chloroform and the combined chloroform extract dried over sodium sulphate and evaporated to dryness under reduced pressure. The residue thus obtained was an oil (90 mg.) that crystallized in contact with a little anhydrous ether. Recrystallized from acetone–ether it consisted of colorless needles, m.p. 189°–190°. Found: C, 63.64; H, 7.44; N, 2.76. Calc. for $C_{26}H_{37}O_8N$: C, 63.52; H, 7.59; N, 2.85%. $[\alpha]_D^{25}$ +131.6° (*c*, 0.38 in chloroform). The compound was very sensitive to alkali and acid and was best purified in neutral solvents. In the ultraviolet it has a maximum, λ_{max} 311 mμ, log ϵ 2.46.

Desmethanol-O-acetyl-anhydrohydroxydelcosine-secodiketone

To a solution of O-acetyl-anhydrohydroxydelcosine-*seco*diketone (200 mg.) in acetic acid (5 ml.), concentrated sulphuric acid (0.5 ml.) was added and the solution heated on the steam bath for 30 minutes. The solution turned pale yellow after 10 minutes and the color deepened slightly towards the end of the heating period. The solution was cooled, neutralized with sodium carbonate, and extracted with chloroform. The residual gum left after evaporation of the chloroform extract was dissolved in benzene and chromatographed on alumina (activity IV). Elution with benzene gave 123 mg. of a base that crystallized from acetone–ether in plates, m.p. 178.5°–179°. Further elution of the column with polar solvents did not yield any crystalline products. For analysis the product was recrystallized three times from the same solvent and dried *in vacuo* at 100°. Found: C, 65.23; H, 7.25; N, 3.11; OCH_3, 13.76. Calc. for $C_{25}H_{33}O_7N$: C, 65.34; H, 7.24; N, 3.05; $2OCH_3$, 13.51%. $[\alpha]_D^{25}$ +76.25° (*c*, 0.8 in chloroform). Ultraviolet: λ_{max} 231–232 mμ, log ϵ 3.89; λ_{max} 312 mμ, log ϵ 2.46. The crystalline desmethanol compound was sensitive to acids and alkalies and with the latter gave a soluble yellow substance which was rapidly oxidized to a tar.

Reduction of Anhydrohydroxydelcosine-secodiketone

A small quantity of the chromatographed amorphous *seco*diketone dissolved in 50%

methanol was treated with sodium borohydride at room temperature for 3 hours. Water was then added and the solution extracted with chloroform. Evaporation of the extract left an oil that crystallized from acetone in plates, m.p. 253°–254°. Found: C, 65.08; H, 8.98; N, 3.34; OCH_3, 16.42. Calc. for $C_{23}H_{37}O_6N$: C, 65.22; H, 8.81; N, 3.31; $2OCH_3$, 14.64%. $[\alpha]_D^{25}$ +34° (*c*, 0.4 in chloroform).

Hydrogenation of Desmethanol-O-acetyl-anhydrohydroxydelcosine-secodiketone

The desmethanol compound (V) (253 mg.) dissolved in 50% acetic acid (8 ml.) was hydrogenated at room temperature and atmospheric pressure in the presence of palladium–charcoal (175 mg.). Two moles of hydrogen were absorbed in 30 minutes and no further uptake was observed during the next 2 hours. The catalyst was filtered out and washed thoroughly with dilute acetic acid. The combined filtrate and washings were neutralized with sodium bicarbonate and extracted with chloroform. The extract on evaporation left a gum (240 mg.) that crystallized when triturated with ether, m.p. 178°–181° (compound VII). Chromatography and further crystallization did not raise the melting point. Found: C, 64.79; H, 7.98; N, 3.19. Calc. for $C_{25}H_{37}O_7N$: C, 64.77; H, 8.05; N, 3.02%. $[\alpha]_D^{25}$ −14° (*c*, 0.75 in chloroform).

Oxidation of Compound VII

The product VII of the catalytic hydrogenation (220 mg.) was dissolved in acetone (20 ml.) containing 50% acetic acid (1 ml.). Powdered potassium permanganate (153 mg.) was added portionwise to the solution over a period of 2 hours. The reaction mixture was allowed to stand at room temperature for 20 hours, excess permanganate destroyed by the careful addition of a saturated solution of sodium bisulphite, and the manganese dioxide filtered off and washed with acetone. The combined filtrate and washings were evaporated under diminished pressure and the residue dissolved in chloroform. The chloroform solution was washed with dilute sulphuric acid and the acid washings extracted once with chloroform. The combined chloroform solutions were dried and evaporated to dryness. There was left a froth which was dissolved in benzene and chromatographed on alumina (activity IV). The fraction eluted with chloroform yielded 130 mg. of the lactam VIII which crystallized from ether – petroleum ether as colorless prisms, m.p. 183°–184°. Found: C, 62.70; H, 7.33; N, 3.08. Calc. for $C_{25}H_{35}O_8N$: C, 62.87; H, 7.39; N, 3.08%. $[\alpha]_D^{25}$ −17° (*c*, 1.1 in chloroform).

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REACTION OF TRICHLOROACETONITRILE WITH PRIMARY AND SECONDARY AMINES

PART I. PREPARATION OF SOME TRICHLOROACETAMIDINES[1]

JOHN C. GRIVAS[2] AND ALFRED TAURINS

ABSTRACT

Trichloroacetonitrile reacts with primary and secondary aliphatic and primary aromatic amines to give N-substituted trichloroacetamidines. A series of N-mono- and N-di-substituted trichloroacetamidines, $CCl_3—C(=NH)(NHR)$ and $CCl_3—C(NR_1R_2)=NH$, was prepared by carrying out the reaction in water, in water–methanol solutions, or in the absence of solvents.

INTRODUCTION

Although acetonitrile forms N-substituted acetamidines by the addition of amines only in the presence of anhydrous aluminum chloride (1), trichloroacetonitrile reacts with amines more easily. The German Patent No. 671,785 (2) reported the preparation of some trichloroacetamidines by the direct interaction of trichloroacetonitrile with aliphatic primary amines at low temperature, without giving any details. Oxley (3) prepared trichloroacetamidine and N,N-ethylene-bis-trichloroacetamidine in benzene solution. Backer and Wanmaker (4) isolated N-methyl- and N-piperidyl-trichloroacetamidine only in the form of picrates. They found that the addition of aromatic amines to trichloroacetonitrile proceeded only in the presence of methanol or acetone. The role of methanol in the reaction was explained by assuming that methanol first adds to trichloroacetonitrile to form an iminoether as an intermediate which subsequently reacts with aniline to give the amidine.

The objective of the present work was the investigation of the preparation of trichloroacetamidines by the direct addition of amines to trichloroacetonitrile without using any catalysts. In the next part, a kinetic study of the reaction will be presented, followed by the investigation of the correlation between the infrared spectra and the structure of amidines.

DISCUSSION

The preparation of the N-substituted trichloroacetamidines involved three general procedures: (*a*) the lower primary and secondary aliphatic amines were treated with trichloroacetonitrile in water solutions; (*b*) the reactions of the higher aliphatic and cyclic amines were carried out in the absence of solvents; and (*c*) the aromatic primary amines were allowed to react with trichloroacetonitrile in water–methanol solution. The results are summarized in Table I. The three procedures are characterized by their simplicity, the absence of catalysts, and the high yields of the reaction products.

The lower aliphatic N-substituted trichloroacetamidines are colorless liquids possessing an unpleasant smell. They can be distilled at low pressure in a dry nitrogen atmosphere, whereas they decompose vigorously on being heated at normal pressure. It was found

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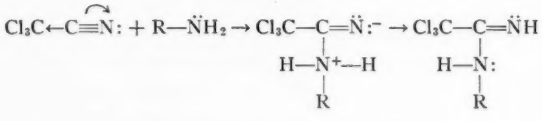
TABLE I

No.	Trichloro-acetamidine	Procedure	Yield, %	B.p.		Empirical formula	Nitrogen, %	
				° C.	mm. Hg		Calc.	Found[j]
1	N-Methyl-[b]	A	86	129	60	$C_3H_5Cl_3N_2$	15.96	15.85
2	N-Ethyl-[c]	A	84	62	2	$C_4H_7Cl_3N_2$	14.77	14.68
3	N-*n*-Butyl-	B	92	71–72	2	$C_6H_{11}Cl_3N_2$	12.87	12.67
4	N-*n*-Amyl-	B	94	89–90	2	$C_7H_{13}Cl_3N_2$	12.09	11.97
5	N,N-Dimethyl-[d]	A	68	51–52	2	$C_4H_7Cl_3N_2$	14.77	14.67
6	N,N-Diethyl-[e]	B	91	61–61.5	2	$C_6H_{11}Cl_3N_2$	12.87	12.69
7	N-Piperidyl-[f]	B	87	80–81	1.5	$C_7H_{11}Cl_3N_2$	12.20	12.09
8	N-Morpholyl-	B	92	89	1	$C_6H_9Cl_3N_2O$	12.10	11.99
9	N-Isopropyl-[g]	B	91	56[a]		$C_5H_9Cl_3N_2$	13.77	13.92
10	N-Benzyl-[h]	B	89	83.5[a]		$C_9H_9Cl_3N_2$	11.13	11.14
11	N-Phenyl-[i]	C	92	101–102[a]		$C_8H_7Cl_3N_2$	11.80	11.80
12	N-*p*-Ethoxyphenyl-	C	94	104[a]		$C_{10}H_{11}Cl_3N_2O$	9.95	9.90
13	N-*p*-Tolyl-	C	92	138.5[a]		$C_9H_9Cl_3N_2$	11.13	10.99
14	N-*m*-Tolyl-	C	95	100[a]		$C_9H_9Cl_3N_2$	11.13	10.96
15	N-*o*-Tolyl-	C	83	73[a]		$C_9H_9Cl_3N_2$	11.13	11.13

[a] *Melting points (° C.), corrected.*
[b] *Picrate, m.p. 163°–164°. Reported in the literature (4): m.p. 163°–164°.*
[c] *Hydrochloride, m.p. 224°–225° (decomp.).*
[d] *The yields can be increased by vigorous stirring for a longer period of time. Picrate, m.p. 162°–163°.*
[e] *Picrate, m.p. 153°.*
[f] *Picrate, m.p. 140°–140.5°. Reported in the literature (4): m.p. 139.5°–140°.*
[g] *The liquid mixture solidified in 2 minutes. The unreacted substances were evaporated in a vacuum and the solid N-isopropyl-2,2,2-trichloroacetamidine was purified by sublimation at 2 mm. pressure.*
[h] *Reported in the literature (2) but no analysis has been given. The substance was crystallized from a methanol–water mixture.*
[i] *The substance has been prepared by other authors (4, 5) using different methods. Hydrochloride, m.p. 180°–183°.*
[j] *Microanalyses by Mr. W. Manser (Herrliberg, Switzerland).*

that the salts of the primary and secondary amines do not react with trichloroacetonitrile in water solution.

The additon of the primary and secondary amines to the carbon–nitrogen triple bond seems to be an ionic reaction, which is facilitated by polar solvents, such as water and methanol. In the absence of kinetic data no proof of the mechanism is possible; however, the information obtained in this work may suggest the following scheme:



The chlorine atoms in the position α to the nitrile group increase the positive charge of the carbon atom of the nitrile group by the inductive (−Is) effect. The attack of the unshared electron pair of the amine nitrogen on the positive carbon is followed by the formation of a bond between these atoms, the liberation of a proton, and the subsequent addition of the proton to the negatively charged nitrogen atom. This scheme may explain the failure of the reaction between the amine salts and trichloroacetonitrile, and also the lower reactivity of the aromatic amines in which the mobility of the unshared electron pair of the nitrogen atom is decreased by the resonance effect. The ionic intermediate also explains the activating influence of water and methanol in the reaction of trichloroacetonitrile with amines.

As has been mentioned above, it has been suggested (4) that methanol is essential in the reaction of trichloroacetonitrile with aniline by forming the intermediate amidine methyl ether. Our experiments indicated that this view cannot stand, for the following reasons: (*a*) aniline reacts with trichloroacetonitrile even in the absence of methanol or other solvents; (*b*) the reaction occurs also in ethanol, which, contrary to methanol, does not react with trichloroacetonitrile.

EXPERIMENTAL

The following procedures were applied for the synthesis of N-substituted trichloroacetamidines.

Procedure A—In Water Solutions

This procedure is useful for commercial aqueous solutions of primary and secondary aliphatic amines.

N-Methyl-2,2,2-trichloroacetamidine.—Trichloroacetonitrile (8 ml.) was added dropwise with stirring over a period of 10 minutes to 15 ml. of 25% aqueous solution of methylamine. The reaction was exothermic and the flask containing the reaction mixture was cooled in an ice-water bath. The lower layer was separated, dried, and distilled. B.p. 129° at 60 mm. pressure. Yield 11.5 g., 86% of the theoretical.

N,N-Dimethyl-2,2,2-trichloroacetamidine.—Trichloroacetonitrile (7.2 g., 0.05 M.) was added to 4 ml. of an aqueous solution of dimethylamine containing 2.25 g. of the pure amine. The mixture was shaken for half an hour. The lower layer was separated, dried, and distilled. B.p. 51°–52° at 2 mm. pressure. Yield 6.45 g., 68% of the theoretical.

Procedure B—In the Absence of Solvents

This procedure can be applied successfully to the reactions of higher aliphatic primary and secondary amines, and also to piperidine and morpholine. The reaction time was 3 hours at least, and the reactions were carried out at room temperature.

N-n-Butyl-2,2,2-trichloroacetamidine.—Trichloroacetonitrile (7.2 g.) was added dropwise to 3.65 g. (0.05 M.) of pure *n*-butylamine. The temperature rose considerably and the mixture turned yellow. The distillation of the reaction product gave a colorless liquid. B.p. 71°–72° at 2 mm. pressure. Yield 9.92 g., 92% of the theoretical.

Procedure C—In Water–Methanol or Methanol Solutions at Room Temperature

This method was applied to the reactions of primary aromatic amines with trichloroacetonitrile. After a period of 3 days the reaction products were precipitated by the addition of water in almost quantitative yields. They were recrystallized from petroleum ether or water–methanol mixtures.

Reaction of Aniline and Trichloroacetonitrile

(*a*) *In the absence of solvents.*—Trichloroacetonitrile (1.44 g., 0.01 M.) was mixed with 0.93 g. of aniline (0.01 M.) and left at room temperature for 5 days. The mixture turned red, brown, and finally black, and after 48 hours crystals started to precipitate in small quantity. The mixture was diluted with 7 ml. of methanol. The reaction product was precipitated by addition of water, filtered, and crystallized from a methanol–water mixture, m.p. 101°–102°. The yield was 1.27 g. (54% of the theoretical).

(*b*) *In ethanol solution.*—Equimolar quantities of the reactants mentioned in (*a*) were dissolved in 5 ml. of ethanol and left at room temperature for 5 days. Addition of water, at the end of this period, caused the precipitation of N-phenyltrichloroacetamidine which melted at 101°–102° after crystallization from water–methanol. Yield 1.8 g. (76%).

Preparation of Picrates and Hydrochlorides

The picrates of trichloroacetamidines were obtained by the addition of equimolar quantities of the amidines and picric acid in benzene solution. The precipitated picrates were crystallized from water. Hydrochlorides of amidines were prepared by passing of a hydrogen chloride gas through solutions of amidines in dry ether.

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SOME NEW SULPHONAMIDES AND DERIVATIVES OF BICYCLIC GUANIDINES[1]

M.-E. KRELING AND A. F. MCKAY

ABSTRACT

The preparations and bacteriostatic activities of some sulphonamide derivatives of the bicyclic guanidines are described. Some 1-(2-hydroxy-3-(aryloxy)propyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazoles have also been prepared.

DISCUSSION

A series of arylsulphonyl derivatives of 2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole (1, 2), Δ^8-hexahydro-1,4,8-pyrimidazole (3), and Δ^9-1,4,9-triazabicyclo(5.3.0)decene (3) have been prepared for evaluation as bacteriostats. Their properties are listed in Table II. An examination of Table I shows that these compounds display bacteriostatic activity against a number of organisms. Moreover, the activity of the 1-*p*-aminobenzenesulphonyl-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole is of the same order as 1-*p*-acetylaminobenzenesulphonyl-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole. Both the *p*-aminobenzenesulphonyl-derivatives are fairly toxic compounds. The LD_{50} values for mice by intraperitoneal injection lie within the range of 100–150 mg./kg.

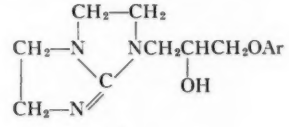
TABLE I

HIGHEST DILUTIONS OF SULPHONAMIDES (MG./ML.) PREVENTING BACTERIAL GROWTH

Test organisms	I*	II	III	IV	V	VI
Staphylococcus pyogenes (R)	4	4	6	3	6	5
Sarcina lutea	3	<2		3	4	1
Streptococcus faecalis	4	5	6	3	6	>5
Aerobacter aerogenes	4	<2	6	3	4	3
Escherichia coli No. 198	3	3	6	3	3	4
Salmonella pullorum	4	4		3	4	4
Pseudomonas aeruginosa	4	5		3	4	4
Proteus mirabilis	5	4		3	4	>5
Proteus vulgaris	3		6	3	5	3
Staphylococcus pyogenes (S)					7	>5

*I, 1-*p*-Acetylaminobenzenesulphonyl-Δ^9-1,4,9-triazabicyclo(5.3.0)decene.
II, 1-*p*-Toluenesulphonyl-Δ^9-1,4,9-triazabicyclo(5.3.0)decene.
III, 1-*p*-Toluenesulphonyl-Δ^8-hexahydro-1,4,8-pyrimidazole.
IV, 1-*p*-Acetylaminobenzenesulphonyl-Δ^8-hexahydro-1,4,8-pyrimidazole.
V, 1-*p*-Acetylaminobenzenesulphonyl-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole.
VI, 1-*p*-Aminobenzenesulphonyl-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole.

Some substituted 2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazoles (I) were prepared by the reaction of 1,2-epoxy-3-aryloxypropanes with 2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imida-



I

Ar = tolyl, *o*- or *p*-chlorophenyl, and 2,4-dichlorophenyl groups

[1]*Manuscript received November 20, 1957.*
Contribution from the L. G. Ryan Research Laboratories of Monsanto Canada Limited, Ville LaSalle, Quebec.

Can. J. Chem. Vol. 36 (1958)

TABLE II

ARYLSULPHONYL DERIVATIVES OF THE BICYCLIC GUANIDINES

Compound	Yield (%)	M.p. (° C.)	Formula	C		H		N		S	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
1-*p*-Toluenesulphonyl-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole	99	182–184	$C_{12}H_{15}N_3O_2S$	54.31	54.36	5.70	5.63	15.84	16.13	12.08	11.84
1-*p*-Acetylaminobenzenesulphonyl-2,3,5,6-tetrahydro-1-imidaz(1,2,-*a*)imidazole	94.5	270–271.5	$C_{13}H_{16}N_4O_3S$	50.61	50.66	5.20	5.26	18.16	18.33	10.40	10.52
1-*p*-Toluenesulphonyl-Δ^8-hexahydro-1,4,8-pyrimidazole	99.5	174–177	$C_{13}H_{17}N_3O_2S$	55.89	56.22	6.13	6.11	15.04	15.12	11.48	11.31
1-*p*-Acetylaminobenzenesulphonyl-Δ^8-hexahydro-1,4,8-pyrimidazole	59.1	267–269	$C_{14}H_{18}N_4O_3S$	52.16	52.30	5.63	5.71	17.39	17.69	9.94	9.95
1-*p*-Toluenesulphonyl-Δ^9-1,4,9-triazabicyclo-(5.3.0)decene	86.5	110.5–111.5	$C_{14}H_{19}N_3O_2S$	57.31	57.12	6.53	6.67	14.32	14.51	10.93	11.16
1-*p*-Acetylaminobenzenesulphonyl-Δ^9-1,4,9-triazabicyclo(5.3.0)decene	72.0	236–238	$C_{14}H_{20}N_4O_3S$	53.55	53.33	5.99	6.13	16.66	16.52	9.54	9.43
1-*p*-Nitrobenzenesulphonyl-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole	97.9 67.0*	179–180 231–233 dec.	$C_{11}H_{12}N_4O_4S$ $C_{17}H_{15}N_7O_{11}S$	44.58 38.86	44.72 38.87	4.08 2.88	4.16 3.11	18.91 18.67	19.36 18.66	10.82 6.10	10.74 6.12
1-*p*-Aminobenzenesulphonyl-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole	85.8	185–186	$C_{11}H_{14}N_4O_2S$	49.60	49.23	5.30	5.36	21.04	21.09	12.04	12.05
1-*p*-Aminobenzenesulphonyl-Δ^9-1,4,9-triazabicyclo(5.3.0)decene	63.0	207–208.5	$C_{13}H_{18}N_4O_2S$	53.05	53.45	6.16	6.40	19.03	18.81	10.90	10.48

**Picrate.*

zole. 1,2-Epoxy-3-(*o*- or *p*-chlorophenoxy)propane gave the expected derivative I (Ar = *o*- or *p*-chlorophenyl) and a small amount (3.8%) of a by-product. The by-product was identified as a di-(2-hydroxy-3-(*o*- or *p*-chlorophenoxy)propyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazolium chloride by analysis. It gave a test for chloride ion and it formed a picrate whose analysis also agreed with this structure. This indicates that the 1,2-epoxy-3-(*o*- or *p*-chlorophenoxy)propane was contaminated with at least 3.8% of the corresponding chlorohydrin derivative, which was most likely used in the preparation of the epoxy compound.

1-(2-Hydroxy-3-(*m*-methylphenoxy)propyl)- and 1-(2-hydroxy-3-(*o*- or *p*-chlorophenoxy)propyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazoles gave LD_{50} values of 125–150 mg./kg. and 150–200 mg./kg. respectively on intraperitoneal injection in mice. These compounds produced convulsions at the toxic level.

EXPERIMENTAL[2]

Preparation of the Arylsulphonyl Derivatives of the Bicyclic Guanidines

Since all of the arylsulphonyl derivatives of the bicyclic guanidines were prepared in the same manner, only the preparation of 1-*p*-toluenesulphonyl-Δ^8-hexahydro-1,4,8-pyrimidazole is described in detail. The properties of the arylsulphonyl derivatives are described in Table II.

To a stirred solution of Δ^8-hexahydro-1,4,8-pyrimidazole (5.0 g., 0.04 mole) and *p*-toluenesulphonyl chloride (7.60 g., 0.04 mole) in water (25 ml.) covered with ether (20 ml.) was added a solution of sodium hydroxide (11 ml. of 3.65 *N* sodium hydroxide solution). After the dropwise addition of the sodium hydroxide solution, which required 20 minutes, the reaction mixture was stirred for an additional 40 minutes at room temperature. The product (11.06 g.) was recovered by filtration and then crystallized from ethyl acetate.

1-p-Aminobenzenesulphonyl-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole

A mixture of 1-(*p*-acetylaminobenzenesulphonyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)-imidazole (9 g., 0.03 mole), ethanol (200 ml.), and 5 *N* sodium hydroxide solution (50 ml.) was heated under reflux for 15 minutes. The solution on cooling and dilution with water deposited crystals, yield 6.7 g. (85.5%). The crude product (m.p. 181°–184°C.) was purified by crystallizing from an acetone–hexane (4:1) solution. 1-*p*-Aminobenzenesulphonyl-Δ^9-1,4,9-triazabicyclo(5.3.0.)decene (Table II) was prepared in a similar manner from 1-*p*-acetylaminobenzenesulphonyl-Δ^9-1,4,9-triazabicyclo(5.3.0)decene.

1-(2-Hydroxy-3-(m-methylphenoxy)propyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole

2,3,5,6-Tetrahydro-1-imidaz(1,2-*a*)imidazole (4.44 g., 0.04 mole) and 1,2-epoxy-3-(*m*-methylphenoxy)propane (6.57 g., 0.04 mole) in absolute methanol (30 ml.) were refluxed for 3½ hours. After the solvent was removed *in vacuo* under nitrogen, a yellow oil was obtained, yield 11.05 g. (99.7%). This oil slowly crystallized over a period of several days. Recrystallization from acetone–hexane gave a 57% yield of pure product (m.p. 102.5°–104° C.). Anal. Calc. for $C_{15}H_{21}N_3O_2$: C, 65.43; H, 7.69; N, 15.27. Found: C, 65.09; H, 7.70; N, 15.42%.

A paper chromatogram of the product on No. 1 Whatman paper developed with butanol – acetic acid – water (40:10:50) gave an R_f value of 0.72±0.01.

Its picrate formed in the usual manner from water melted at 127°–132° C., yield

[2]*All melting points are uncorrected. The microanalyses were determined by Micro-Tech Laboratories, Skokie, Illinois.*

85.8%. One crystallization from absolute ethanol raised the melting point to 143.5°–144° C. Anal. Calc. for $C_{21}H_{24}N_6O_9$: C, 50.00; H, 4.79; N, 16.66. Found: C, 50.10; H, 4.67; N, 16.92%.

1-(2-Hydroxy-3-(o- or p-chlorophenoxy)propyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole

To a solution of 2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole (4.44 g., 0.04 mole) in absolute methanol (35 ml.) was added 1,2-epoxy-3-(*o*- or *p*-chlorophenoxy)propane (7.35 g., 0.04 mole) and the mixture was refluxed for 3 hours. Evaporation of the solution *in vacuo* gave 11.7 g. (99%) of semicrystalline solid. A paper chromatogram on No. 1 Whatman paper, which was developed with butanol – acetic acid – water (40:10:50) solvent, gave two spots on spraying with bromcresol green solution with R_f values of 0.77 ± 0.01 and 0.88. The two components were separated by crystallization from acetone. An acetone-insoluble fraction was obtained with an R_f value of 0.88, yield 0.78 g. (3.8%). Two crystallizations from methanol – ethyl acetate (1:5) solution raised the melting point from 183°–189° C. to a constant value of 190°–191° C. These crystals gave a positive test for chloride ion with silver nitrate solution. The analytical values agreed with those calculated for a di-(2-hydroxy-3-(*o*- or *p*-chlorophenoxy)propyl)-2,3,5,6-tetrahydro-1-imidaz-(1,2,-*a*)imidazolium chloride. Anal. Calc. for $C_{23}H_{28}Cl_3N_3O_4$: C, 53.46; H, 5.46; Cl, 20.58; N, 8.13. Found: C, 53.53; H, 5.53; Cl, 20.83; N, 8.01%.

A picrate (m.p. 162.5°–164° C.) was formed in 80% yield in the usual manner from water. The melting point was not changed by further crystallization. Anal. Calc. for $C_{29}H_{30}Cl_2N_6O_{11}$: C, 49.09; H, 4.26; Cl, 9.99; N, 11.85. Found: C, 49.01; H, 4.32; Cl, 10.06; N, 11.89%.

The acetone filtrate from above on cooling deposited 8.37 g. (71.2%) of crystals melting at 149°–153° C. Three crystallizations from acetone raised the melting point to 153.5°–154° C. (R_f, 0.77 ± 0.01). Anal. Calc. for $C_{14}H_{18}ClN_3O_2$: C, 56.86; H, 6.13; Cl, 11.99; N, 14.21. Found: C, 57.32; H, 6.02; Cl, 12.12; N, 14.52%.

A picrate (m.p. 127°–128° C.) was formed in the usual manner from water, yield 86.2%. Two crystallizations from methanol–ether (1:1) solution raised the melting point to 129°–130° C. Anal. Calc. for $C_{20}H_{21}ClN_6O_9$: C, 45.77; H, 4.03; Cl, 6.76; N, 16.02. Found: C, 46.12; H, 4.19; Cl, 6.95; N, 16.14%.

1-(2-Hydroxy-3-(2,4-dichlorophenoxy)propyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole

A solution of 2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole (4.44 g., 0.04 mole) and 1,2-epoxy-3-(2,4-dichlorophenoxy)propane (8.79 g., 0.04 mole) in absolute methanol (35 ml.) was refluxed for 3 hours. Evaporation of the solution gave 13.04 g. (98.7%) of dark viscous oil. A paper chromatogram prepared as described above gave two basic spots with R_f values of 0.77 and 0.46. The latter value indicated the presence of unchanged 2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole.

The crude oil (11.04 g.) was refluxed with water (25 ml.) and the aqueous phase was removed by decantation. This process was repeated twice to remove the unchanged starting material from the product. After the sticky residue was triturated with acetone (50 ml.), crystallization occurred, yield 2.36 g. (17.9%). The melting point of these crystals was raised from 154°–156.5° C. to 155°–156.5° C. (R_f, 0.77) by crystallizing from ethanol–water (2:3) solution. Anal. Calc. for $C_{14}H_{17}Cl_2N_3O_2$: C, 50.92; H, 5.19; Cl, 21.48; N, 12.73. Found: C, 50.96; H, 5.23; Cl, 21.83; N, 12.34%.

The picrate was prepared by dissolving a sample of the crystals in the minimum amount of methanol and adding saturated aqueous picric acid solution. The picrate (m.p. 144°–146° C.) was obtained in 66% yield. It was purified to a constant melting point

of 146°–147° C. by crystallizing from methanol–ether (2:1) solution. Anal. Calc. for $C_{20}H_{20}Cl_2N_6O_9$: C, 42.95; H, 3.61; Cl, 12.68; N, 15.03. Found: C, 42.84; H, 3.59; Cl, 13.03; N, 14.85%.

ACKNOWLEDGMENT

The bacteriostatic and acute toxicity values were determined by Drs. H. A. Baker and C. Chappel of Ayerst, McKenna, and Harrison Ltd., Montreal.

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VOLTAIC CELLS IN FUSED SALTS

PART III. THE SYSTEM SILVER - SILVER CHLORIDE, CADMIUM - CADMIUM CHLORIDE[1]

S. N. FLENGAS[2] AND T. R. INGRAHAM

ABSTRACT

Using a silver – silver chloride reference electrode, the standard electrode potential has been established for the equilibrium $Cd|Cd^{++}$ in melts containing equimolar quantities of KCl and NaCl. The experimentally obtained standard potential was greater than that calculated from theoretical thermodynamic data. This difference was attributed to the formation of a cadmium complex in the melt. A dissociation constant for the complex was calculated.

The effect of temperature on the electromotive force of the silver–cadmium voltaic cell was also measured, and the heat of the cell reaction was calculated from the data. To extend the temperature range of the cadmium data, a cadmium–lead alloy was used in the higher temperature experiments. To correlate these data with those for the pure cadmium system, the activity coefficients of cadmium in the alloy were determined electrometrically using the silver – silver chloride electrode as a reference. It was found that the activity coefficients were in agreement with previously published data obtained at lower temperatures using a pure cadmium reference electrode. The activity coefficients were virtually independent of temperature but showed large positive deviations from unity when the mole fraction of cadmium was decreased below about 0.8.

INTRODUCTION

Parts I and II of this series (1, 2) described the development and use of a reversible silver – silver chloride reference electrode for determining the electromotive forces of voltaic cells in chloride melts at high temperatures.

In this paper, experiments will be described in which the silver – silver chloride reference electrode was used to study the cadmium – cadmium chloride equilibria. An equimolar mixture of molten potassium and sodium chlorides was used as the common solvent.

These results are an additional contribution to the current program of establishing electromotive series for metals in molten salts at different temperatures.

EXPERIMENTAL

The technique used to study the Cd–Ag system was essentially the same as that previously described (1). During the preliminary experimental work it became apparent that because of the relatively high vapor pressure of molten cadmium and the inflammability of cadmium vapor in air, a closed cell operating with an inert atmosphere would be required. The complete cell design is shown in Fig. 1. The cell was constructed from silica tubing of 2 in. diameter and consisted of two sections connected by a ground silica joint. The upper section of the cell was closed with a cork stopper, into which were fitted the silver – silver chloride reference electrode, the thermocouple well, the feeding pipe with stirrer, and the gas inlet tube. The cork stopper was covered externally with Pyseal cement and then water-cooled to prevent the melting of the cement from the heat of the furnace. The inner surface of the cork stopper was covered with a close-fitting layer of asbestos. The lower section of the cell was used as a container for the molten metal indicator electrode and the molten salts. Electrical contact with the indicator electrode was made by means of a tungsten wire sealed into silica tubing and dipped into the metal pool.

[1]*Manuscript received December 31, 1957.*
Contribution from the Mineral Dressing and Process Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa. Published with the permission of the Director, Mines Branch, Ottawa.
[2]*National Research Council Postdoctorate Fellow assigned to the Mines Branch.*

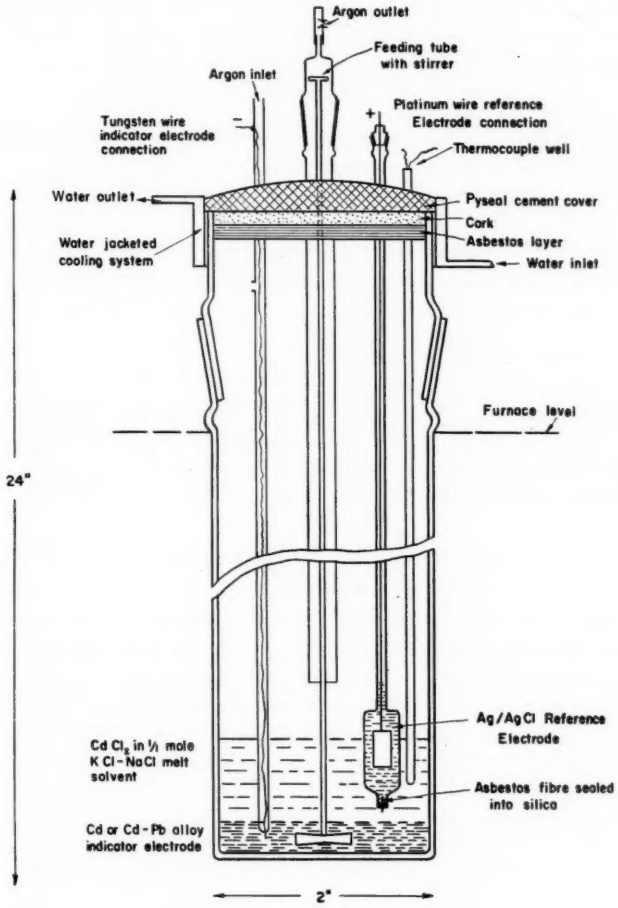

FIG. 1. All silica cell.

For potential measurements at temperatures below the boiling point of cadmium (767° C.), the indicator electrode was either pure molten cadmium metal or cadmium–lead alloy. At temperatures above 767° C., a high boiling point cadmium–lead alloy was used to determine the electromotive forces over a range of temperature in excess of 100 Centigrade degrees and thus clearly establish the linearity of the data.

To protect the contents of the cell from the atmosphere, purified argon was introduced continuously into the cell and released through a small Bunsen valve. The slight positive pressure of argon in the cell protected the contents completely over the full course of runs lasting up to 2 days.

The voltaic cell used during the experiments may be represented as follows:

$$\underset{(-)}{M} \mid \underset{\text{(indicator electrode)}}{CdCl_2\ (x_2)\ \text{KCl–NaCl (1/1 mole)}} \parallel \text{Asbestos fiber} \parallel \underset{\text{(reference electrode)}}{AgCl\ (x_1)\ \text{KCl–NaCl (1/1 mole)}} \mid \underset{(+)}{Ag}$$

where M is cadmium or a cadmium-lead alloy, and x_1 and x_2 are, respectively, the mole fractions of AgCl and $CdCl_2$ in the alkali chloride melt solvent. The cell reaction in an ideal solution should be:

$$Cd + 2Ag^+ = Cd^{++} + 2Ag.$$

The relationship between the electromotive force and the metal-ion concentration in the experimental cell is given by the Nernst equation in the form:

$$E_{cell} = (E^\circ_M - E^\circ_{Ag}) - (2.303RT/2\mathcal{F}) \log(x_2/x_1^2 a_m) \quad [1]$$

where E°_M and E°_{Ag} are, respectively, the standard electrode potentials of the half-cells $M/CdCl_2$ and $Ag/AgCl$ under the conditions of the experiment, and a_m represents the activity of cadmium in the metallic electrode. For pure cadmium, $a_m = 1$.

Determination of Metal Activities in Alloys

The use of equation [1] for the calculation of standard electrode potentials requires a knowledge of the activity (a_m) of cadmium in the cadmium–lead alloy. Since the activities of cadmium in this alloy were known only for temperatures up to 570° C. (3), it was necessary to determine these values experimentally at higher temperatures. This was done by calculating the electromotive force, ΔE, of the following hypothetical metal-alloy concentration cell:

$$Cd \left| \begin{matrix} CdCl_2\ (x) \\ KCl\text{–}NaCl\ (1/1\ mole) \end{matrix} \right| Cd(a_m)\text{–}Pb.$$

This electromotive force was derived from the difference between the potential of the experimental cell using the cadmium–lead alloy as an indicator electrode, and that of the same cell when using pure cadmium metal. The alloy was prepared *in situ* by adding small pieces of 99.9% lead to the molten cadmium electrode, or, when the equilibrium was to be approached from the pure lead side, by adding small pellets of 99.99% cadmium to the molten lead electrode. The alloy electrodes were homogenized by a small stirrer inserted through the feeding tube of the cell. The activity of cadmium in the alloy was then calculated by the equation:

$$\Delta E = 2.303RT/2\mathcal{F} \log(1/a_m). \quad [2]$$

RESULTS AND DISCUSSION

The electromotive force of the cadmium cell was measured first as a function of the metal-ion concentration and then as a function of temperature. The results of the experiments in which the concentration of the metal ion was varied at constant temperature are shown in Table I.

From equation [1] it follows that the relationship between E_{cell} and $\log(x_2/x_1^2)$ should be linear; and that when x_1 and x_2 are chosen so that the log term of this equation becomes zero, then

$$E_{cell} = E^\circ_M - E^\circ_{Ag}.$$

When the electromotive forces of the cells were plotted against $\log(x_2/x_1^2)$, as calculated from the experimental data given in Table I, the results were well represented by a straight line in agreement with the theory, as shown in Fig. 2. The slope of the experimental line agrees well with the theoretical values calculated from equation [1] for a two-electron electrode reaction. The results of these calculations are given in Table II.

TABLE I

ELECTROMOTIVE FORCES OF THE Cd–Ag VOLTAIC CELL AS A FUNCTION OF THE CADMIUM-ION CONCENTRATION IN THE INDICATOR ELECTRODE AT 680° C.

$$\begin{array}{l|l||l|l} \text{Cd} & \text{CdCl}_2 \text{ in 1/1 mole} & \text{AgCl in 1/1 mole} & \text{Ag} \\ (-) & \text{KCl–NaCl} & \text{KCl–NaCl} & (+) \end{array}$$

Mole fraction of AgCl (x_1)	Mole fraction of $CdCl_2$ (x_2)	E_{cell} (volts)
6.235×10^{-2}	2.309×10^{-3}	0.625
"	4.481×10^{-3}	0.598
"	9.047×10^{-3}	0.568
"	1.488×10^{-2}	0.550
"	2.568×10^{-2}	0.528
"	4.807×10^{-2}	0.497
"	8.348×10^{-2}	0.472

Also included in Table II are values for the standard electrode potential of cadmium derived graphically from Fig. 2. For comparison, the standard potential calculated from thermodynamic data given by Hamer, Malmberg, and Rubin (4) is also included.

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED RESULTS FOR THE Cd–Ag ELECTRODE SYSTEMS

		$E°_M - E°_{Ag}$ (volts)		Slope	
Cell reaction	$t°$ C.	Exptl.	Theor.	Exptl.	Theor.
$Cd + 2Ag^+ = Cd^{++} + 2Ag$	680	0.604	0.420	0.097	0.094

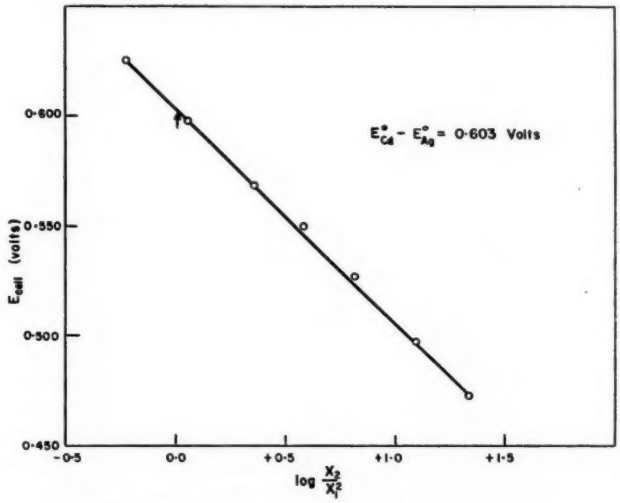

FIG. 2. Electromotive forces of the cells:

$$\begin{array}{l|l||l|l} \text{Cd} & \text{CdCl}_2 & \text{AgCl } (x_1 = 6.235\times10^{-2}) & \text{Ag} \\ (-) & \text{KCl–NaCl (1/1 mole)} & \text{KCl–NaCl (1/1 mole)} & (+) \end{array}$$

as a function of $\log(x_2/x_1^2)$ at a constant temperature of 680° C.

It is of theoretical interest to compare the experimentally obtained standard potential of the voltaic cell with the theoretical value calculated from the thermodynamic data. If the difference is entirely attributed to the presence of a cadmium complex in the alkali chloride melt solvent, the dissociation constant, K_d, of the complex can be calculated, using the method previously described (1):

$$K_d \text{ (Cd complex)} = 1.17\times10^{-2}.$$

The magnitude of this value indicates the presence of a fairly stable cadmium complex in the melt.

The effects of temperature change on the electromotive forces of the cadmium–lead alloy – silver and the cadmium–silver voltaic cells were investigated next. The results are shown in Table III and Fig. 3. (The procedure by which the activity a_m and the standard electrode potentials included in Table III were obtained will be described later in the text.)

TABLE III

EFFECT OF TEMPERATURE ON THE ELECTROMOTIVE FORCE OF THE CELLS

(*a*) Cd (−) | $CdCl_2$ ($x_2 = 3.875\times10^{-2}$) KCl–NaCl (1/1 mole) ‖ AgCl ($x_1 = 6.103\times10^{-2}$) KCl–NaCl (1/1 mole) | Ag (+)

T (° K.)	E_{cell} (volts)
933	0.5255
955	0.5132
980	0.5015
1000	0.4921
1025	0.4784

(*b*) Cd(a_m)–Pb (−) | $CdCl_2$ ($x_2 = 3.785\times10^{-2}$) KCl–NaCl (1/1 mole) ‖ AgCl ($x_1 = 6.103\times10^{-2}$) KCl–NaCl (1/1 mole) | Ag (+)

where $x_m = 0.4754$ and $a_m = 0.7654$

On heating			On cooling		
T (° K.)	E_{cell} (volts)	$E°_{Cd} - E°_{Ag}$ (volts)	T (° K.)	E_{cell} (volts)	$E°_{Cd} - E°_{Ag}$ (volts)
982	0.493	0.568	1025	0.456	0.537
984	0.479	0.557	1011	0.463	0.544
991	0.474	0.553	997	0.472	0.552
1012	0.466	0.546	985	0.476	0.555
1033	0.454	0.536	973	0.482	0.560
1065	0.438	0.523	957	0.490	0.565
1084	0.432	0.518	947	0.494	0.569
			937	0.498	0.572
			935	0.502	0.576

It is of interest to note, in Fig. 3, that the two straight lines which express the relationship between the electromotive force of the foregoing cells and temperature are essentially parallel. This shows that the activity of cadmium in a cadmium–lead alloy is almost independent of temperature. The results of experiments to determine the activities a_m of cadmium in a cadmium–lead alloy at one temperature (680° C.) are shown in Table IV. The activity coefficients were calculated using the well-known equation:

$$a_m = x_m\gamma_m \qquad [3]$$

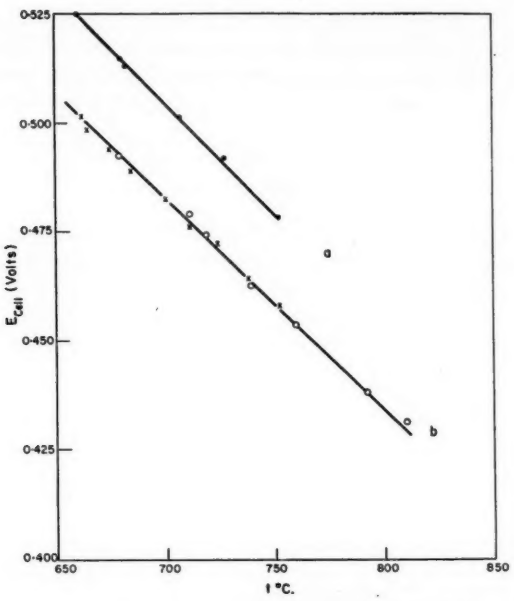

FIG. 3. The effect of temperature on the electromotive forces of the following cells:

(*a*) $\underset{(-)}{\text{Cd}} \mid \text{CdCl}_2\ (x_2 = 3.785\times10^{-2}) \mid\mid \text{AgCl}\ (x_1 = 6.103\times10^{-2}) \mid \underset{(+)}{\text{Ag}}$
KCl–NaCl (1/1 mole) KCl–NaCl (1/1 mole)

(*b*) $\underset{(-)}{\text{Cd}(a_m = 0.7654)\text{–Pb}} \mid \text{CdCl}_2\ (x_2 = 3.785\times10^{-2}) \mid\mid \text{AgCl}\ (x_1 = 6.103\times10^{-2}) \mid \underset{(+)}{\text{Ag}}$
KCl–NaCl (1/1 mole) KCl–NaCl (1/1 mole)

○ with increasing temperature, × with decreasing temperature.

TABLE IV

MEASUREMENTS OF THE ACTIVITY OF CADMIUM METAL IN THE CADMIUM–LEAD ALLOY AT 680° C.

$\underset{(-)}{\text{Cd}(x_m)\text{–Pb}} \mid \text{CdCl}_2\ (x_2 = 3.285\times10^{-2}) \mid\mid \text{AgCl}\ (x_1 = 6.103\times10^{-2}) \mid \underset{(+)}{\text{Ag}}$
KCl–NaCl (1/1 mole) KCl–NaCl (1/1 mole)

Mole fraction of cadmium (x_m)	E_{cell} (volts)	ΔE (volts)	Activity (a_m) of cadmium metal in the alloy	Activity coefficient (γ_m)
1.000	0.4985	−0.0000	1.0000	1.000
0.9495	0.4956	−0.0029	0.9315	0.981
0.8602	0.4920	−0.0065	0.8535	0.992
0.7873	0.4900	−0.0085	0.8128	1.032
0.6883	0.4916	−0.0069	0.8453	1.228
0.5664	0.4910	−0.0075	0.8537	1.507
0.4718	0.4878	−0.0107	0.7709	1.634
0.4712	0.4870	−0.0115	0.7551	1.602
0.3426	0.4768	−0.0217	0.5889	1.719
0.2331	0.4665	−0.0320	0.4585	1.967
0.1434	0.4524	−0.0461	0.3251	2.266
0.0801	0.4353	−0.0632	0.2143	2.675

where x_m is the mole fraction of cadmium in the alloy and γ_m is the activity coefficient.

In Table IV it can be seen that at high cadmium concentrations the cadmium–lead

alloy behaves essentially ideally. Below a mole fraction of about 0.8, deviations from ideality increase and activity coefficients greater than unity are obtained.

The variation of the activity with the mole fraction of cadmium in the cadmium–lead alloy is shown in Fig. 4.

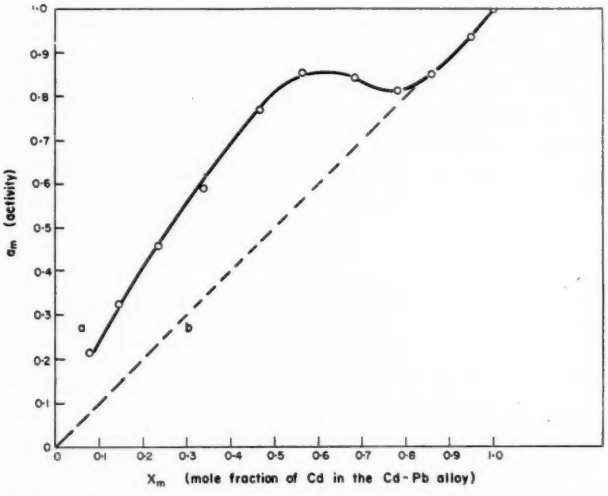

FIG. 4. The variation of the activity of cadmium in the Cd–Pb alloy, with the mole fraction of cadmium at 680° C. (*a*) Experimental data; (*b*) theoretical line for an ideal alloy.

The activity coefficient values obtained in the present investigation for a temperature of 680° C. are in good agreement with values given in the literature for lower temperatures. This is shown in Table V, where activity coefficients calculated from the data given by Taylor (3) are tabulated together with values obtained in the present investigation.

TABLE V

ACTIVITY COEFFICIENTS OF CADMIUM METAL IN CADMIUM–LEAD ALLOY AT VARIOUS TEMPERATURES AND CONCENTRATIONS

Mole fraction of cadmium in the alloy	Activity coefficient (γ_m)				
	432° C.	480° C.	544° C.	572° C.	680° C.*
0.2	2.50	2.35	2.15	2.10	2.50
0.4	1.75	1.68	1.58	1.57	1.65
0.6	1.48	1.48	1.44	1.44	1.50

* *Values obtained in the present investigation.*

It will be observed that temperature change has a very small effect on the values of the activity coefficients. This is in agreement with the previous observations on temperature effects in Fig. 3. The two lines are essentially parallel and the difference between the values of the respective electromotive forces corresponds to a $(2.303RT/2\mathcal{F})\log a_m$ term, where a_m is the activity of the cadmium in the alloy at the lower temperature of 680° C.

Having established the activities of cadmium in a cadmium–lead alloy, it was possible to use equation [1] to calculate the standard electrode potential of cadmium ($E^\circ_{Cd} - E^\circ_{Ag}$) at different temperatures from the data in columns 1 and 2 of Table III(*b*). From these standard potentials, using the well-known equations

$$\Delta F^\circ = -nE^\circ\mathcal{F}, \qquad [4]$$

$$\Delta F^\circ = -2.303RT \log K,$$

the equilibrium constant for the cell reaction given in Table II was calculated for various temperatures. The results of these calculations are shown in Fig. 5, where log K was plotted against the reciprocal of the absolute temperature. The curve is linear over the

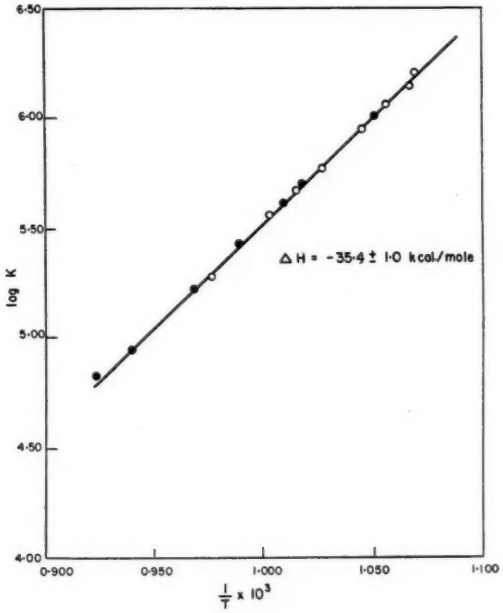

FIG. 5. The variation of log K with the reciprocal of temperature for the system:
$Cd(a_m = 0.7654)$–Pb | $CdCl_2$ ($x_2 = 3.785\times10^{-2}$) KCl–NaCl (1/1 mole) || AgCl ($x_1 = 6.103\times10^{-2}$) KCl–NaCl (1/1 mole) | Ag
(−) (+)
○ with increasing temperature, ● with decreasing temperature.

temperature range investigated, and the best straight line through the experimental points was calculated by applying the least squares method. The heat of reaction (ΔH_r), which is the difference between the heats of formation of the respective chlorides in the melt solvent, i.e.

$$\Delta H_r = \Delta H_{f(CdCl_2 \text{ in KCl–NaCl})} - \Delta H_{f(AgCl \text{ in KCl–NaCl})}, \qquad [5]$$

can be calculated from the slope of the straight line in Fig. 5, in accordance with the van't Hoff equation,

$$d \ln K/dT = \Delta H_r/RT^2. \qquad [6]$$

The result thus obtained is:

$$\Delta H_r = -35.4 \pm 1.0 \text{ kcal.}$$

It will be noted that this value includes any effect due to the presence of the solvent.

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THE EFFECT OF THE AMBIENT GASES ON THE SURFACE PHOTOCURRENT IN ANTHRACENE[1]

T. C. WADDINGTON[2] AND W. G. SCHNEIDER

ABSTRACT

Following the observation that the photocurrent in anthracene is markedly affected by an atmosphere of oxygen over the system, the behavior of anthracene in the presence of atmospheres of other gases has been investigated. The effect has been shown to be confined to the surface photocurrent, and the active gases have been shown to fall into two classes: (1) gases which are electron acceptors, e.g. BF_3, HCl, O_2, and NO, which all *increase* the photocurrent markedly; (2) gases and vapors which are electron donors, e.g. NH_3, $(CH_3)_2O$, and $(CH_3)_3N$, which all *decrease* the photocurrent markedly. The effect of the pressure of the ambient gas and of the temperature of the system on the photocurrent has also been investigated.

INTRODUCTION

Though the photoconductivity of anthracene was observed as early as 1913 by Volmer (1) it was not until the last decade that systematic investigations of its behavior were undertaken. It was recognized by Vartanyan (2) that the photoconductivity of a polycrystalline layer of anthracene was markedly affected by oxygen in contact with it, the photoconductivity being decreased on hard pumping. These observations were confirmed in this laboratory by Chynoweth (3), who transferred his attention to single crystals, because of the difficulty of outgassing multicrystalline layers and therefore of obtaining meaningful and reproducible results. The effect of oxygen on the photoconductivity of crystalline anthracene was also investigated by Bree, Carswell, and Lyons (4), working with sublimation flakes.

In view of the effect of oxygen it was decided to study the effect of other gases and vapors on the photocurrent in anthracene single crystals. A brief, preliminary account (5) of this work, which is reported here in greater detail, has already appeared. About the same time a note was published by Bree and Lyons (6) on the effect of oxygen, nitric oxide, and sulphur dioxide on the photoconductivity of anthracene. Subsequently a note (7) has appeared reporting the effects of temperature on the photoconductivity in the presence of oxygen.

EXPERIMENTAL

The photoconductivity cell was similar to that described by Chynoweth and Schneider (8). The gases used were obtained commercially and were of high purity. The nitrogen and argon were spectroscopically pure. The anthracene used in growing the crystals employed in the above experiments was purified by continuous chromatography in the manner described by Sangster and Irvine (9). Two types of crystals were employed. Large crystals were cut from long single crystals kindly grown for us by Dr. Lipsett in a Bridgeman-type furnace. Sublimation flakes were grown in an atmosphere of argon. Electrodes were painted onto the crystals with aquadag.

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Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada.
Issued as N.R.C. No. 4679.
[2]*National Research Laboratories Postdoctorate Fellow, 1955–56. Present address: Gonville and Caius College, Cambridge, England.*

RESULTS

(*a*) *Effects of Gases on the Photocurrent in the Sandwich Cell*

Using a sandwich cell of polycrystalline anthracene Chynoweth (3) observed a large effect, with oxygen, on the photocurrent. Working with single crystals he found only a 20% to 30% increase over the hard-vacuum level of the photocurrent. In order to see if the presence of oxygen or other gases at the illuminated face of the crystal had any effect on the true bulk photocurrent in anthracene, an earthed guard ring was placed on the edge of the sandwich cell and the photocurrent measured *in vacuo* and in the presence of oxygen and of other gases. In no case could any change in the level of the photocurrent be detected. It was concluded that the gases only affected the current flowing in the surface layers of the crystal and all subsequent observations were made using the surface-cell arrangement.

(*b*) *Surface Cell—Equilibrium Behavior*

(1) *Qualitative account of the effects of various gases.*—The gases BF_3, HCl, SO_2, NO, and O_2 on admission to the photocell were all found to increase the photocurrent in the surface arrangement to a steady value well above the hard-vacuum value. Typical increases were by a factor of 20. The gases and vapors NH_3, $(CH_3)_3N$, $(CH_3)_2O$, $(C_2H_5)_2O$, C_2H_5OH, H_2O, and $(CH_3)_2CO$ were all found to decrease the photocurrent to a steady value below that of the high-vacuum value. Typical decreases were by a factor of 5 to 10. The gases and vapors CO_2, N_2, A, CH_4, and $(CH_3)_4C$ were found to have no effect on the level of the vacuum photocurrent.

(2) *The effect of the pressure of ambient gas on the level of the surface photocurrent.*—The dependence of the photocurrent on the pressure of oxygen gas has already been reported by Bree and Lyons (6). Our results are in agreement with theirs. The pressure dependence has the shape of a Langmuir adsorption isotherm, and a plot of the photocurrent minus its hard-vacuum value, i.e., $i_p - i_{vac}$, against the pressure, p, is initially linear. A plot of $p/(i_p - i_{vac})$ against p gives a good straight line. This was also found to be the case for BF_3 and HCl.

The dependence of the photocurrent on gas pressure was also studied in the presence of ammonia, of trimethylamine, and of acetone vapor. A plot of the hard-vacuum value minus the value found in the presence of ammonia, i.e., $i_p - i_{vac}$, against the pressure, p, resembled a Langmuir adsorption isotherm, being initially linear and saturating in the usual manner. A plot of $p/(i_p - i_{vac})$ against p gave a good straight line. Similar results were obtained for trimethylamine. A plot of $i_p - i_{vac}$ for acetone does not give a Langmuir isotherm, the shape of the curve resembling more nearly that for multilayer adsorption. The plots of $i_p - i_{vac}$ against p and $p/(i_p - i_{vac})$ against p are shown in Figs. 1 and 2, respectively, for BF_3 and NH_3.

(3) *The effect of temperature on the level of the surface photocurrent in the presence of an ambient gas.*—The effect of temperature (in the range $-130°$ to 55° C.) on the value of the photocurrent in the surface and sandwich cell in a hard vacuum has been reported in a previous communication (10). It takes the form of an exponential relation $i = i_0 \exp(-E/RT)$. In the presence of an ambient gas such as O_2 or BF_3 the behavior falls into two classes:

(*a*) In the case where the pressure is above the saturation value for the Langmuir isotherm, e.g., $p > p_{sat}$, the behavior is exactly the same as in the case of the hard vacuum.

(*b*) In the case where the pressure is below the saturation value for the Langmuir isotherm, e.g., $p < p_{sat}$, the behavior is different to the hard-vacuum case and the

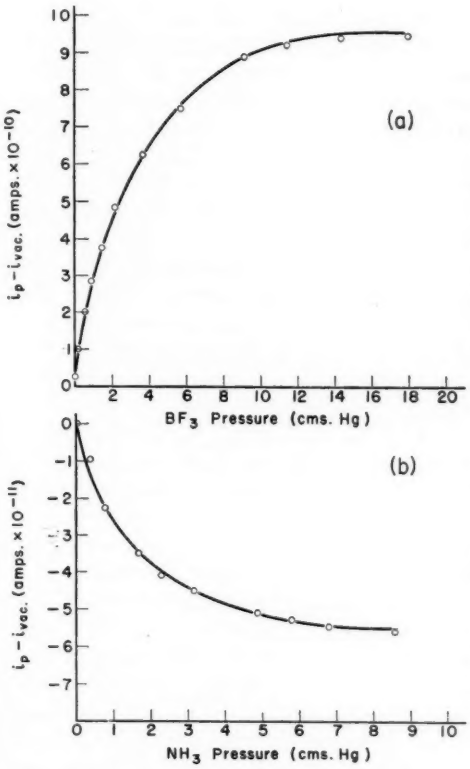

FIG. 1. (*a*) Increase of photocurrent of anthracene as a function of BF_3 gas pressure. (*b*) Decrease of photocurrent of anthracene as a function of NH_3 gas pressure.

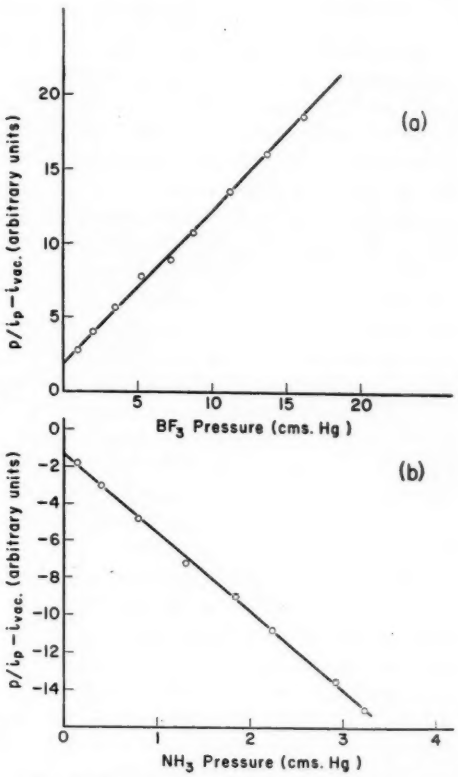

FIG. 2. Plot of $p/(i_p - i_{vac})$ vs. p for (*a*) BF_3 and (*b*) NH_3 on anthracene single crystals.

photocurrent temperature relation cannot be fitted to a simple $i = i_0 \exp(-E/RT)$ relationship.

(4) *Effect of wavelength on the photocurrent in the presence of an ambient gas.*—Some experiments were carried out on the effect of oxygen on the wavelength dependence of the photocurrent. No significant change could be found, the wavelength dependence in the surface cell showing the same type of behavior in each case.

(*c*) *Surface Cell—Non-equilibrium Behavior*

Though the effect of the ambient gases on the photocurrent is generally very rapid, there are one or two cases where the photocurrent takes an appreciable while to reach its equilibrium value. This is particularly noticeable in the case of SO_2, where several hours are required in the dark for the photocurrent to rise to a steady value after the admission of the gas to the cell. The rise is much more rapid when the crystal is illuminated than when it is in the dark. Over the somewhat limited range with which it was possible to work with SO_2 the effect was markedly dependent on temperature, the rise time being shortened by a rise in temperature.

DISCUSSION

Though at the moment sufficient information, theoretical or experimental, is not available for a detailed mechanism of the effects of ambient gases on the photoconductivity of anthracene to be given, certain definite generalizations can be made and some tentative suggestions advanced. The most important first point is that though anthracene possesses both a surface and a bulk photocurrent only the surface photocurrent is affected by the adsorbed gases. Secondly, since the wavelength dependence of the surface photocurrent is not altered by the adsorbed gases, they probably do not affect the process of carrier formation but only the movement of charge carriers.

The gases in class two, water vapor, ammonia, dimethyl ether, trimethylamine, etc., appear to be only weakly adsorbed. This is shown by the ease with which the photocurrent can be restored to its vacuum level by pumping. All these gases are electron donors of varying power, all possessing lone pairs, and they all reduce the photoconductivity. The gases in class one, oxygen, nitric oxide, boron trifluoride, etc., are all strongly adsorbed, probably chemisorbed. This is indicated by the difficulty of pumping them off the crystal as indicated by a return of the photocurrent to its hard-vacuum value. The photocurrent–pressure behavior can be fitted to a Langmuir adsorption isotherm. These gases must be interacting strongly with the π-electrons of the surface anthracene molecules, either because they possess acidic protons, e.g. HCl, or because they have a vacant orbital of low energy, e.g. boron trifluoride.

Other evidence, presented elsewhere (10), suggests that the majority charge carriers in anthracene are positive holes. Many other photoconductors show an effect due to ambient gases on the surface photocurrent and this behavior is usually explained in terms of the effect on the surface energy levels of the crystal by the gas (11, 12, 13). However, none of these materials, such as germanium, zinc sulphide, and cadmium sulphide, are as sensitive as anthracene is to the effect of adsorbed gases. If it is assumed that on the surface of an anthracene crystal *in vacuo* the energy levels of the positive-hole band are lower than in the bulk of the crystal and that the effect of the ambient gas is to raise or lower the energy levels at the surface depending on whether the gas is an electron donor or an electron acceptor relative to anthracene, then a simple phenomenological explanation is given of the behavior outlined in this paper. It is also interesting to note that if the above explanation is the correct one then the surface semiconductivity of anthracene and similar crystals might very well be expected to be affected by the presence of adsorbed gases. Pick and Wissman (14) have studied the semiconductivity of napthalene crystals and report that the pre-exponential factor and the energy of activation are altered by the presence of oxygen, the conductivity being increased.

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NUCLEAR MAGNETIC RESONANCE MEASUREMENTS OF PROTON TRANSFERS IN ACETYLACETONE IN DIETHYLAMINE AND TRIETHYLAMINE[1]

L. W. REEVES[2] AND W. G. SCHNEIDER

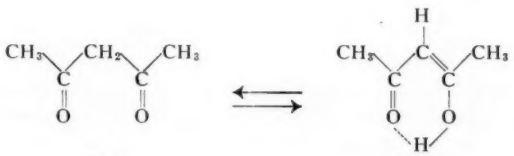
ABSTRACT

Solutions of acetylacetone in triethylamine are completely enolic at all dilutions studied (0.1 to 0.85 mole fraction). The nature of the proton resonance signals in the NMR spectrum indicates a proton exchange between the OH and =CH— groups of the enol tautomer. Addition of diethylamine to acetylacetone results in the formation of a white crystalline 1:1 molecular complex which melts at 41.5° C. The NMR spectrum of the complex reveals a simultaneous proton exchange between the amine NH group and the OH and =CH— groups of the enol tautomer. The mechanism of this exchange is discussed. In effect the addition of amines to acetylacetone not only alters the keto–enol equilibrium very markedly, but also increases the keto–enol conversion rate. With diethylamine the conversion rate becomes sufficiently high to "average out" the individual NMR spectra of the two tautomers.

INTRODUCTION

The proton magnetic resonance technique provides a fruitful method for investigating systems capable of undergoing keto–enol conversion. Typical of such systems is acetylacetone, for which the keto–enol equilibrium may be represented as follows:

[1]



Keto Enol

The conversion rate between the two tautomers is sufficiently slow so that the NMR spectrum of acetylacetone, under ordinary conditions, shows separate and distinct proton signals of both the keto and enol tautomers. Hence from the relative intensities of the signals the equilibrium concentrations of each of the two tautomers can be determined (1, 2). The proton resonance spectrum of acetylacetone together with the assignment of the individual proton signals is reproduced in Fig. 1.

In the sense that the keto–enol conversion involves a transfer of a proton from a carbon atom to an oxygen atom, the process may be regarded as a proton exchange phenomenon. Depending on the rate of proton exchange, the shape of the proton resonance signals may be modified in a characteristic way. If we consider a simple example of a proton capable of exchanging between two sites, A and B, we may define lifetimes, τ_A and τ_B, which are a measure of the mean time that the proton spends at each site. When the exchange is slow two separate proton signals appear in the NMR spectrum corresponding to the different environment of the proton at each of the two sites. If the rate of exchange is increased, as for example by raising the temperature, then the two proton signals may be observed to broaden, and eventually at even higher rates of exchange, to coalesce to a single averaged signal at an intermediate position.

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Issued as N.R.C. No. 4689.
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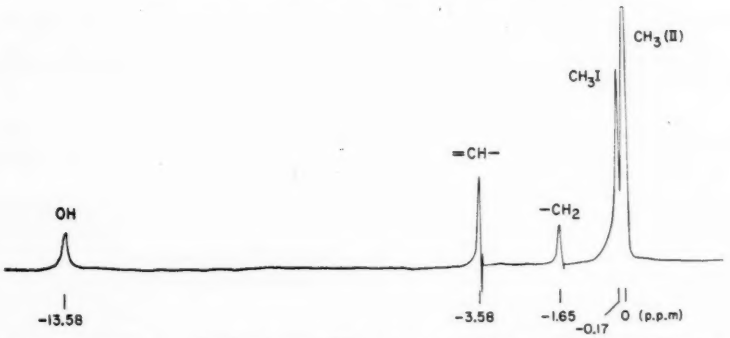


FIG. 1. Proton resonance spectrum of pure acetylacetone at 40 Mc./s. Chemical shifts are shown in p.p.m. Reading from left to right (low field to high field) the signal assignment is respectively: enol OH group, enol =CH— group, keto —CH_2— group, keto CH_3 groups, and enol CH_3 groups.

The general problem of proton exchange between two sites has been treated by Gutowsky and co-workers (3, 4, 5). If the separation of the two signals when the exchange is slow is $2\pi(\nu_A-\nu_B)$, where ν_A and ν_B are the resonance frequencies of the proton at each of the two sites, then under certain simplifying assumptions the condition for coalescence of the two signals is

$$[2] \qquad \tau \leqslant \sqrt{2}/[2\pi(\nu_A-\nu_B)],$$

where $\tau = \frac{1}{2}\tau_A = \frac{1}{2}\tau_B$. This type of behavior can be observed, for example, in a 2:1 alcohol–water mixture. At room temperature two proton signals corresponding to the two different OH groups are observed, which when the temperature is raised gradually broaden and coalesce to a single signal at 72° C. (6).

Returning to the acetylacetone system, it may be noted that the separation* of the OH signal of the enol form and the —CH_2— signal of the keto form in frequency units is ~480 c./s. Thus to obtain a coalescence or averaging of these signals would require τ to be of the order of 5×10^{-4} seconds. The lifetime of the keto and enol tautomers is evidently much greater than this. Attempts to increase the conversion (exchange) rate sufficiently by heating and thus to produce a single averaged spectrum for the two tautomers were unsuccessful. When the temperature was raised to 150° C. no indication of signal coalescence, or even a noticeable signal broadening, was apparent. However, as described in the present paper, addition of triethylamine or diethylamine to acetylacetone not only disturbs the keto–enol equilibrium in a profound way, but also substantially alters the keto–enol conversion rate such that under certain conditions an "averaged" proton spectrum is observed.

EXPERIMENTAL

The method of purification of the acetylacetone used in the present work has been described previously (2). Diethylamine and triethylamine were redistilled once from C.P. material.

The proton resonance measurements were made with a V-4300 Varian high resolution spectrometer operating at a fixed frequency of 40 Mc./s. A device which was used for simultaneously spinning and heating the samples, contained in 5-mm. o.d. glass tubes, has been described elsewhere (7).

**For a measuring frequency of 40 Mc./s.*

RESULTS

In a previous paper (2) it was reported that acetylacetone in solution in triethylamine is completely converted to the enol tautomer. Solutions of acetylacetone in triethylamine, studied in the range 0.1 to 0.85 mole fraction acetylacetone, gave rise to proton resonance spectra which, in addition to the signals of the amine, showed only the three signals characteristic of the enol tautomer (cf. Fig. 1). It was observed, however, that the signals arising from the OH group and the =CH— group *both* showed pronounced broadening, suggesting an exchange behavior involving these protons. If this were so, heating the solution should cause further broadening and ultimate coalescence of the two signals when the exchange rate is sufficiently high. Fig. 2 shows NMR traces of the

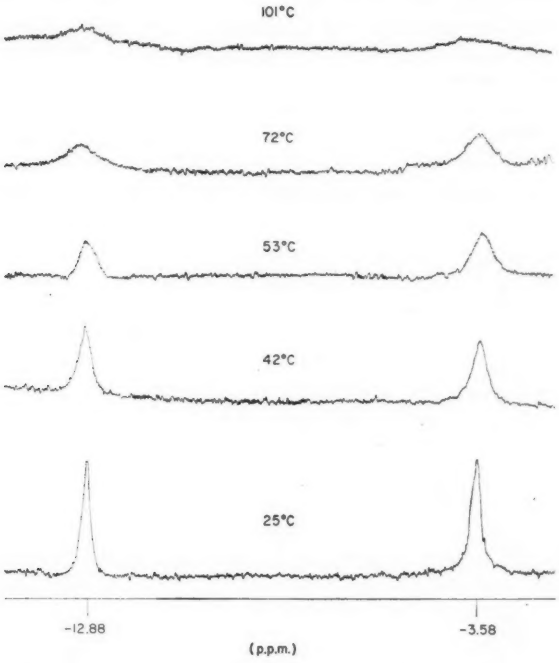


FIG. 2. NMR traces of the enol OH and =CH— group signals of acetylacetone (mole fraction 0.316) in triethylamine at various temperatures.

OH and =CH— signals of a solution of acetylacetone (mole fraction 0.316) in triethylamine at various temperatures. The increased signal broadening is evident. The solution was heated to 165° C. At this temperature the signals became so broad as to be lost in the background noise, and of course under these conditions it is difficult to avoid signal saturation. The coalesced signal, which requires still higher rates of proton exchange, must therefore appear at a much higher temperature. A further solution containing 0.703 mole fraction acetylacetone was also investigated. Apart from some chemical shift displacements in the spectrum, the same features were observed.

From the relative broadening of the signals as a function of temperature, shown in

Fig. 2, rate constants can be determined, permitting an evaluation of the activation energy for the proton exchange process. For this purpose we may employ the simple relation*

$$1/T_2' = 1/T_2 + 1/2\tau,$$

where $1/T_2'$ is related to the half-width of the broadened signal, $1/T_2$, to the corresponding half-width in the absence of exchange, and 2τ is the mean lifetime of the proton at either site. Thus, assuming negligible exchange at 25° C., values of τ at each temperature can be derived from the broadened signals. The results yield an activation energy of approximately 8 kcal./mole for the exchange process. This value is rather inaccurate, however, because of partial signal saturation broadening at the higher temperatures.

Diethylamine affects the keto–enol conversion to a much greater extent than triethylamine. In solutions of acetylacetone in diethylamine, as with triethylamine, no signals which could be assigned to the keto tautomer appear in the NMR spectrum. A specific molecular interaction between diethylamine and acetylacetone is indicated by the formation of a 1:1 molecular compound, with evolution of heat, when the two substances are mixed in equimolar quantities. The molecular complex is a white crystalline solid melting at 41.5° C. Both the amine and acetylacetone can be recovered from the complex. The complete binary freezing-point diagram of the diethylamine–acetylacetone system is shown in Fig. 3.

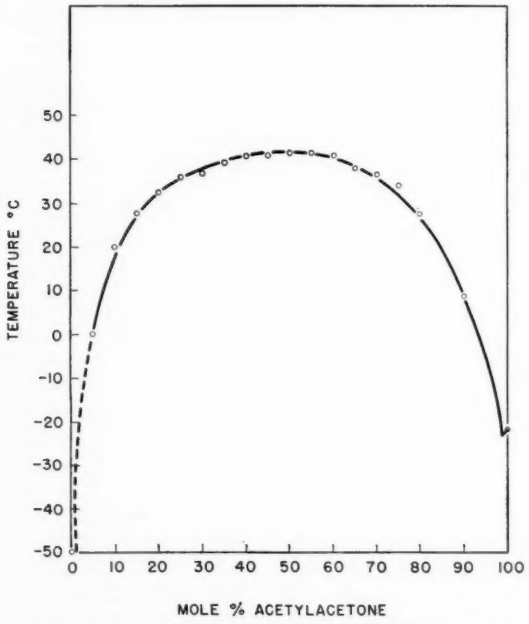


FIG. 3. The binary freezing-point diagram of acetylacetone and diethylamine.

*As pointed out by Professor H. S. Gutowsky (private communication), this relation follows from Eq. (3) of Ref. (5) with the assumption of slow exchange and no overlap of the two component signals. The derivation and application of this relation has been discussed by Grunwald, Lowenstein, and Meiboom, J. Chem. Phys. **27**, 630 (1957).

The NMR spectrum of the 1:1 complex at a temperature just above the melting point (where a partial dissociation may be expected) is reproduced in Fig. 4. The chemical

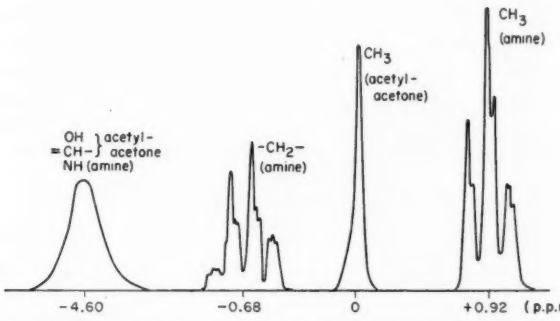


FIG. 4. NMR spectrum of 1:1 acetylacetone–diethylamine mixture (~43° C.). Chemical shifts are shown in p.p.m. The individual resonance signals were recorded at different receiver gain. The relative intensities are therefore not comparable.

shift and assignment of the individual signals are given. Thus after the two signals arising from the ethyl group of the amine are allowed for, the spectrum of the acetylacetone contains but two signals. The sharp signal on the high-field side, which was used as the reference signal in measuring the chemical shifts, must be assigned to the methyl groups of the acetylacetone. This leaves the rather broad signal at low field to account for the signals arising from the OH and =CH— groups of the enol tautomer,* as well as the NH group of the amine. The broad, structureless nature of this signal suggests that all three of these groups are simultaneously exchanging protons. This expectation was indeed confirmed by observing the proton resonance spectrum of the complex dissolved in CCl_4 at a concentration of about 15 mole per cent of complex. The spectrum was similar to that of Fig. 4 except that the low-field signal was now split into two signals having relative intensities 2:1. These two signals, shown in Fig. 5, confirm the assignment of the low-field signal in Fig. 4 as arising from *three* protons, since a 2:1 intensity ratio of the decomposed signal must involve at least three protons. Of the two signals (Fig. 5) the one at higher field, with intensity 1, can be assigned to the

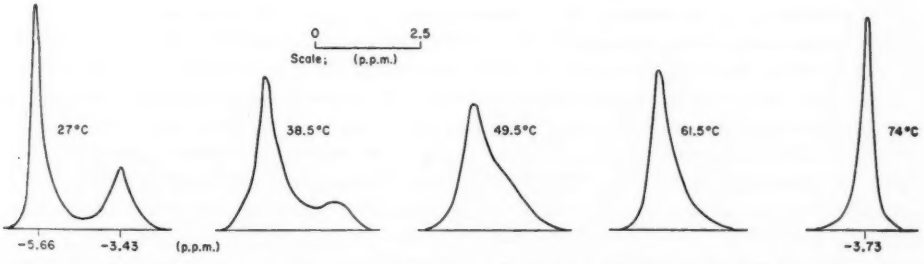


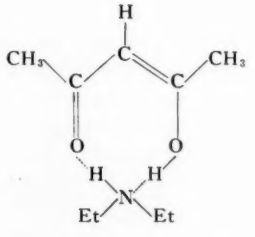
FIG. 5. NMR traces at various temperatures of the enol OH and diethylamine NH groups (low-field signal) and of the enol =CH— group (high-field signal) from 15 mole per cent solution of the 1:1 acetylacetone–diethylamine complex in CCl_4.

**This assumes, by analogy with the behavior in triethylamine, the acetylacetone spends most of its time as the enol tautomer.*

enol =CH— group, since it appears at very nearly the same position as the corresponding signal in the spectrum of acetylacetone in triethylamine. The lower field signal with intensity 2 must then be assigned to the OH group and the NH group of the amine. This observed pattern of signals suggests that these two groups are rapidly exchanging protons, but the exchange of these protons with the =CH— group is much slower when the system is diluted in CCl_4 than in the pure molecular complex of acetylacetone and diethylamine. However, as shown in Fig. 5, heating the CCl_4 solution causes an increase in the exchange rate and a coalescence of the separate signals, at which point all three protons are again undergoing rapid exchange with each other.

INTERPRETATION OF RESULTS

The most striking and perhaps surprising feature of the results is the involvement of the =CH— group of the enol tautomer in a rapid proton exchange with the OH group and also with the NH group of the diethylamine. In triethylamine, which lacks the latter group but does possess a basic N atom, this exchange is evidently considerably slower. In the presence of either amine the enol tautomer of acetylacetone predominates, suggesting a preferred interaction between the amine and this tautomer. This interaction is undoubtedly through hydrogen bonds. The internal hydrogen bond in the enol tautomer may be expected to become disrupted in the presence of the strong donor N atom of the amine, the OH group then tending to form a bond with the N atom. In general, proton exchange is greatly favored in strong hydrogen bonds, the hydrogen bond providing the exchange path (6). On this basis a fast exchange between the enol OH group and the NH group of the diethylamine can be understood in terms of hydrogen-bonded structures such as the following:



which permits a rapid transfer of protons between oxygen and nitrogen.

A simultaneous rapid exchange of the =CH— group proton under certain conditions, as indicated by the NMR results, is rather more difficult to interpret. It does in fact appear that such an exchange must take place via the keto tautomer as a short-lived intermediate state. A plausible mechanism, which can be illustrated with the aid of a molecular model shown in Fig. 6, is the following. The model of the enol tautomer in the figure shows a configuration in which the internal hydrogen bond has been broken and the OH group is rotated out of the molecular plane. In this configuration the OH proton finds itself adjacent to two electron donor sites. One electron donor site is represented by the electron lone pair of the carbonyl oxygen atom, the other by the olefinic π-bond. There is now ample evidence that the π-electrons in such bonds can act as electron donor sites for molecular interactions with H—X acceptor groups (8, 9, 10). Accordingly in the above configuration of the enol form, conditions are favorable for the NH group of a neighboring amine molecule to orient itself such that the OH group can form a hydrogen

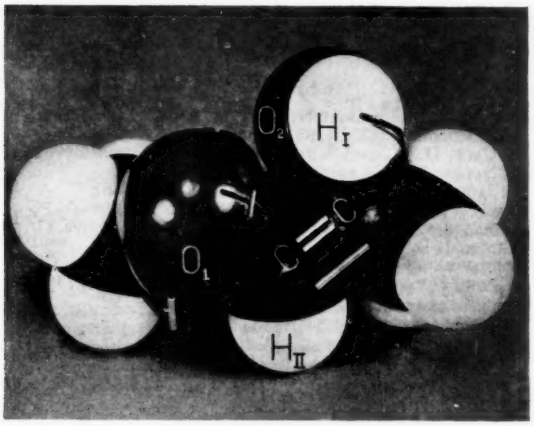


FIG. 6. Molecular model of the enol tautomer of acetylacetone.

bond to the donor lone pair electrons of the N atom, and the H atom of the NH group can bond to either of two donor sites, the carbonyl oxygen atom or the π-bond. This then permits rapid proton exchange among all sites. The individual proton exchanges taking place may be represented by:

(1) $OH\cdots N \longleftrightarrow O\cdots H{-}N$

(2) $H_{II}{-}C(=C)\cdots H{-}N \longleftrightarrow H_{II}{-}C(-C)-H_I\cdots N$

Enol Keto

(3) $H_{II}{-}C(=C)\cdots H{-}O \longleftrightarrow H_{II}{-}C(-C)-H_I\cdots O$

Enol Keto

Process (1) may be expected to be rapid under all conditions. Process (3) is simply the ordinary keto–enol conversion and both (2) and (3) involve the keto tautomer as an intermediate "exchange" state. However the lifetime of this state must be small, since no separate signals corresponding to the keto form are observed in the NMR spectra of the amine solutions. This together with the relatively weak donor property of the π-bond of the enol form would account for the observed lower probability of processes (2) and (3) relative to that of (1). These processes are nevertheless sufficiently rapid to average out the separate spectra of the two tautomers. The spectrum of acetylacetone in diethylamine shown in Fig. 4 can in fact be regarded as an averaged spectrum of the two tautomers. It will be noted, however, that formation of the keto tautomer as a short-lived intermediate state permits the protons H_I and H_{II} to become equivalent, and accordingly both can take part in the exchange process. In this way the exchange of the enolic $=CH-$ group (proton$_{II}$) can be accounted for.

The conclusion indicated by the present study is that amines, by virtue of strong hydrogen bonding interactions with acetylacetone, not only alter the keto–enol equilibrium very extensively, but also greatly increase the keto–enol conversion rate. The conversion rate is more rapid in diethylamine than in triethylamine, presumably because the latter lacks an exchangeable proton of its own.

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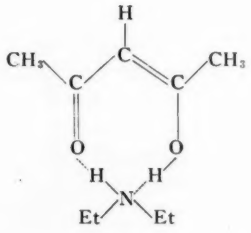

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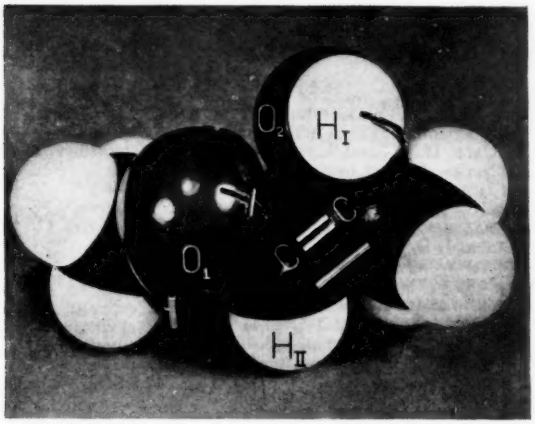

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(3) $H_{II}{-}C(=C)\cdots H{-}O \longleftrightarrow H_{II}{-}C(-C){-}H_I\cdots O$

Enol Keto

Process (1) may be expected to be rapid under all conditions. Process (3) is simply the ordinary keto–enol conversion and both (2) and (3) involve the keto tautomer as an intermediate "exchange" state. However the lifetime of this state must be small, since no separate signals corresponding to the keto form are observed in the NMR spectra of the amine solutions. This together with the relatively weak donor property of the π-bond of the enol form would account for the observed lower probability of processes (2) and (3) relative to that of (1). These processes are nevertheless sufficiently rapid to average out the separate spectra of the two tautomers. The spectrum of acetylacetone in diethylamine shown in Fig. 4 can in fact be regarded as an averaged spectrum of the two tautomers. It will be noted, however, that formation of the keto tautomer as a short-lived intermediate state permits the protons H_I and H_{II} to become equivalent, and accordingly both can take part in the exchange process. In this way the exchange of the enolic $=CH-$ group (proton$_{II}$) can be accounted for.

The conclusion indicated by the present study is that amines, by virtue of strong hydrogen bonding interactions with acetylacetone, not only alter the keto–enol equilibrium very extensively, but also greatly increase the keto–enol conversion rate. The conversion rate is more rapid in diethylamine than in triethylamine, presumably because the latter lacks an exchangeable proton of its own.

The authors are indebted to Mr. Yves Lupien for carrying out the freezing-point measurements.

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THE INFRARED SPECTRA OF 4-SUBSTITUTED-THIOSEMICARBAZIDES AND DIAZOTIZATION PRODUCTS[1]

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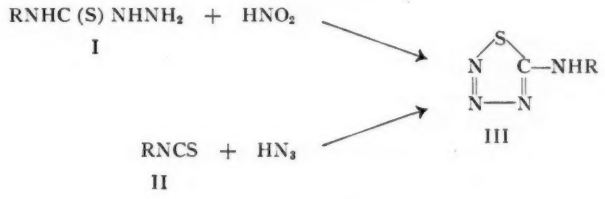
ABSTRACT

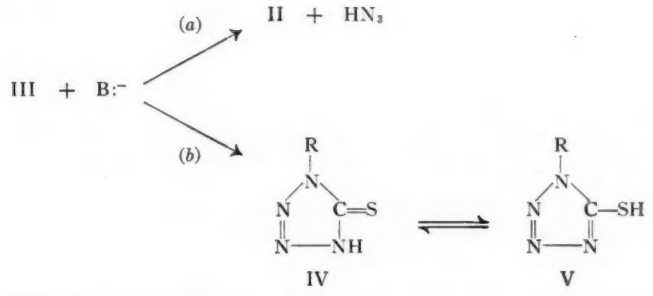
The infrared absorption spectra of 4-substituted-thiosemicarbazides, 5-(substituted)amino-1,2,3,4-thiatriazoles, and the corresponding isomeric tetrazolinethiones have been studied and structural assignments of importance to these systems made or suggested. Important conclusions drawn from the spectral data are: there is no suggestion of any thiol–thione tautomerism for the solid 4-substituted-thiosemicarbazides and that the thione structure predominates for these substances; that the so-called 5-thiol-tetrazoles also exist as thiones; and that the diazotization products of the 4-substituted-thiosemicarbazides yield 1,2,3,4,-thiatriazoles rather than the isomeric open chain thiocarbamyl azides. The C=S, —N—C=S, and cyclic —N—N=N— configurational assignments, which are of importance to the classes of compounds studied, are discussed.

INTRODUCTION

In a previous communication, Lieber, Pillai, and Hites (1) reported that the reaction of 4-alkyl- or 4-aryl-thiosemicarbazides, I, with nitrous acid, as well as the reaction of alkyl- or aryl-isothiocyanates, II, leads to the identical 5-(substituted)amino-1,2,3,4-thiatriazoles, III:

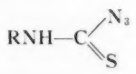


The 5-(substituted)amino-1,2,3,4-thiatriazoles (III) on treatment with base undergo two competitive reactions (1):



[1]*Manuscript received January 13, 1958.*
Contribution from the Departments of Chemistry of DePaul University and the Armour Research Foundation of the Illinois Institute of Technology, Chicago, Illinois.
[2]*DePaul University, Chicago 14, Illinois, U.S.A., to whom all requests for reprints and additional information should be addressed.*
[3]*DePaul University.*
[4]*Armour Research Foundation.*

the extent of mode (*a*) or (*b*) depending on the electronegativity of the substituent R.* One of the invaluable aids in treading through the pathways of these reactions involved the application of infrared absorption spectroscopy (1). Thus the chemistry of the 5-(substituted)amino-1,2,3,4-thiatriazoles, III, could be explained in terms of the isomeric thiocarbamyl azide structure, VI:



VI

except for the fact that III shows a complete absence of the azido-group frequencies in the infrared region (1). This communication reports the infrared absorption data obtained on structures I, III, and IV obtained in the course of the investigation summarized above.

EXPERIMENTAL

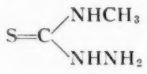
The spectra were recorded on a Perkin-Elmer single-beam spectrometer (Model 12C) with sodium chloride prism. The positions of the absorption maxima are listed in Tables I, II, and III with the intensities being indicated by the following symbols: s, strong; m, medium; w, weak; vw, very weak; and v, variable. The compounds studied were those reported upon in the previous communication (1). The spectra were taken in Nujol mulls.

DISCUSSION

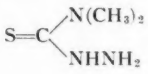
4-Substituted-thiosemicarbazides

All of the important absorption bands of the 4-substituted-thiosemicarbazides in the region 1640–780 cm.$^{-1}$ are summarized in Table I. No SH band was found in these compounds in the region 2600–2500 cm.$^{-1}$, the range in which the SH stretching vibrations are most likely to appear (2). This clearly shows that there is no thiol–thione tautomerism in these compounds in the solid state:

A similar conclusion has been drawn by Bogomolov and co-workers (3). All of the compounds studied showed N—H stretching modes of vibration. In general, the important infrared absorption frequencies of the 4-substituted-thiosemicarbazides can be summarized as in Table IV. The bands due to the hydrazino-, —$NHNH_2$, portion of the structure have been assigned on the basis of studies presented by Randall (4) and Lieber (5). Both the 4-methyl-, (VII) and 4,4-dimethyl- (VIII) thiosemicarbazides:



VII



VIII

show weak absorption at 1439 cm.$^{-1}$ and 1447 cm.$^{-1}$, respectively. In agreement with Bellamy (2) these bands can be assigned to the C—H deformation mode in N—CH_3 but do not seem to be too closely defined to afford any useful correlation. The medium or

**More recently it has been found that for III (R = alkyl) a third mode of decomposition can also take place in alkaline media involving an internal oxidation–reduction leading to the formation of nitrogen, sulphur, and further degradation products. This work will be reported in a separate communication.*

TABLE I

INFRARED SPECTRA OF 4-SUBSTITUTED-THIOSEMICARBAZIDES

$R_1R_2NC(S)NHNH_2$

R_1	R_2	NH_2[a]	N—C=S	C=S	NH_2[c]	—	NH[d]	NH_2[e]	NH[f]
H	H	1642s 1619s	1524s	1362[b]	1280w	1155m	—	996s	800m
CH_3	H	1639s	1555s	1361[b]	1263s	1166m	1081m 1053m	971s	—
CH_3	CH_3	1608s	1506s	1353s	1263w	1155m	1062m	977s	—
C_2H_5	H	1632s	1540s	—	1268s	1162s	1085m 1055s 1037s	976s 934s	807m 773s
n-C_4H_9	H	1630s	1540s	1336[b]	1266s	1212s 1160m	1112w 1089m 1055s	942m	800m 738m
n-C_7H_{15}	H	1634s	1536s	1361[b]	1259s	1232m 1156w	1087w 1062m	956m	781m
$C_6H_5CH_2$	H	1610s	1488s	1370s	1266w	1227m 1188w	1076m	957s	791m
CH_2=$CHCH_2$	H	1631s	1538s	1361[b]	1272s	1232w	1094w 1070m	988w 963m	778m
C_6H_5	H	1634s	1522s	1361[b]	1279s	1212m	1065s	969s	774w
4-ClC_6H_4	H	1631s	1527s	1395w	1264s	1205s	1078s	980m	815w
2-$CH_3OC_6H_4$	H	1618s	1536s	1346w	1266s	1195m 1163w	1058m 1048m	969m	792m
4-$CH_3C_6H_4$	H	1620s	1540s	1334[b]	1300w	1198s 1118w	1060s	976s 928w 910s	842m 810s

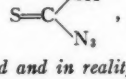
[a] *Deformation-asymmetric.*
[b] *Seen as a shoulder on the mineral oil peak (single-beam).*
[c] *Deformation-symmetric.*
[d] *Rocking.*
[e] *Rocking.*
[f] *Bending.*

weak intensity bands observed in the region 1232–1155 cm.$^{-1}$ may be ascribed to the C—N stretching vibration (2, 4). Ueno (6) has recently assigned the region 1300–1273 cm.$^{-1}$ to the C—N stretching vibration of the para-amino group of azobenzenes. In addition to the absorption bands discussed above, bands due to other functional groups and substituted aromatic rings were also observed.

5-(Substituted)amino-1,2,3,4-thiatriazoles

The most significant observation arising out of this study of the infrared absorption spectra of a series of fourteen 5-(substituted)amino-1,2,3,4-thiatriazoles, summarized in Table II, is the absence of an absorption band in the region 2170–2080 cm.$^{-1}$. This rules out (1, 7) the presence of an azido group, supporting structure III and eliminating from consideration structure VI as proposed by Olivari-Mandala (8). Recent studies (9) have confirmed the strong absorbance for the azido group which occurs with great consistency close to 2130 cm.$^{-1}$. This intense N≡N asymmetric stretching absorption is so strong and so little altered by environmental groups as to make its absence in an infrared spectrum a guarantee that the compounds under scrutiny are free of this structural entity.* As

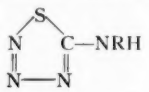
Lieber, Pillai, Ramachandran, and Hites (J. Org. Chem. **22, 1750 (1957)) have recently shown that the reaction products of azide ion and carbon disulphide, which have long been regarded in the literature (Audrieth, Chem. Revs. **15**, 169 (1934)) as derivatives of azidodithiocarbonic acid,*



show no azido group frequency in the infrared and in reality are derivatives of the 1,2,3,4-thiatriazole ring system.

TABLE II

INFRARED ABSORPTION MAXIMA OF
5-(SUBSTITUTED)AMINO-1,2,3,4-THIATRIAZOLES



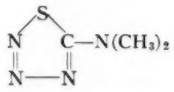
R =	Absorption bands, cm.$^{-1}$																		
H	1724m	1618s		1506m					1333w	1297w	1264w	1233w	1161w	1111m		1053m		943m	889w
CH_3	1695w		1582s					1395m		1282m		1225w		1104s		1031s		933m	
C_2H_5			1545s							1300s			1198m	1150w	1082m	1053m	932w		892w
n-C_4H_9	1724m		1538s							1290m	1247m		1181m	1144w	1086m	1053w		935s	903w
n-C_7H_{15}	1724m		1538s							1294m	1247w		1171w	1142w	1092w	1059w		935m	
CH_2=$CHCH_3$	1718w		1558s	1524s					1323w	1280m		1225w	1174m	1136w	1096m	1055w	990m	940m	911w
$CH_3(H$=$CH_3)$			1560s			1441w	1404m		1318m	1297m	1248w	1217s		1085m		1058m		951s	905s
$C_6H_5CH_2$			1539s			1440s		1370s	1348s	1292s		1220m	1168m		1093s	1032w	963w	934m	
C_6H_5		1605s	1560s		1497m					1289m		1238w	1193m	1155w	1093s	1030w	962w	946w	892w
4-$CH_3C_6H_4$	1721m	1613s	1563s	1513m						1282m		1235w	1198m	1149w	1105s	1032w	962w	950w	909w
2-$CH_3C_6H_4$	1721w	1604s	1588m	1527s	1488w	1458s				1288m				1112w	1076s				
4-$CH_3OC_6H_4$		1605m	1563m	1508s		1453s				1292m	1243s		1175w		1083m	1032m			
2-$CH_3OC_6H_4$		1608w	1588m	1539s	1486s	1464s	1411m		1325m	1292m		1236s	1171w	1117s	1084s	1047w		940w	
						1440s										1026s			
4-Cl—C_6H_4		1618s	1560s		1493s		1422m			1295m		1233w	1200s	1100s		1005w	960w		870w
													1183w						

additional confirmation of the assigned structure the characteristic absorptions for C=S and —N—C=S are also absent (Table II).

A number of the 5-(substituted)amino-1,2,3,4-thiatriazoles exhibit a band of weak or medium intensity in the region 1724–1695 cm.$^{-1}$. Randall (4) found a strong absorption band in the region 1695–1664 cm.$^{-1}$ for guanidine. Lieber (5) reported a strong absorption band in the region 1681–1661 cm.$^{-1}$ for a series of guanidine derivatives. In a few cases a band was observed a few hundredths of a micron on either side of this region. Kumler (11) repeated the infrared spectral studies of Lieber (5) on a more limited number of nitroguanidine derivatives and reported bands in the region 1663–1618 cm.$^{-1}$. All investigators (2, 4, 5, 10, 11, 12) are in agreement in assigning these bands to the C=N stretching frequency, the unit occurring in imine-type structures, >C=N—, i.e. in an open chain. Randall (4) assigned a strong 1697 cm.$^{-1}$ band to open-chain C=N linkage in N-carbethoxybenzalhydrazone and a strong band at 1694 cm.$^{-1}$ to C=N$^+$ type of linkage in phenaceturiminomethyl ether hydrochloride. It is therefore possible that the moderate to weak band in the region 1724–1695 cm.$^{-1}$ in 1,2,3,4-thiatriazole derivatives is due to an external C=N linkage. This could arise by a tautomeric shift of a proton as in structures III to IX:

III IX

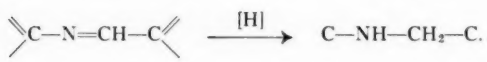
the intensity of the band depending upon the ratio of IX to III. In dimethylamino-1,2,3,4-thiatriazole, X:



X

this tautomeric shift is not possible and the band at 1724–1695 cm.$^{-1}$ is missing, although no firm conclusion can be drawn from this since the band is also missing in those thiatriazole derivatives in which tautomeric shifts are possible.

All of the compounds listed in Table II exhibit a strong intensity band between 1618 and 1525 cm.$^{-1}$. Bellamy (2) assigns a band of variable intensity in the region 1660–1480 cm.$^{-1}$ for the C=N stretching vibration in conjugated cyclic compounds. Since the —N=N— absorption is generally weak and variable it is unlikely that the band in the 1618–1525 cm.$^{-1}$ region is due to —N=N— stretching. Ueno (6) examined a series of 17 azobenzenes and assigned the —N=N— stretching frequency to two bands of variable intensity in the 1455–1400 cm.$^{-1}$ region. On the other hand, when the nitrogen atom of the C=N bond is so substituted that it is able to take on a polar character, the characteristic frequency alters considerably. Goulden (13) quotes the region of 1659–1510 cm.$^{-1}$ for situations of this type. More recently, Clougherty (14) examined the infrared spectra of aromatic Schiff bases and ascribed the band of medium intensity in the 1631–1613 cm.$^{-1}$ region to the conjugated C=N stretching frequency. Of considerable interest is the fact that this band disappeared on reduction of the Schiff base to a secondary amine:



On the basis of chemical and ultraviolet spectral evidence Lieber (1) suggested that 5-(substituted)amino-1,2,3,4-thiatriazoles may possibly exist in the so-called mesoionic form, XI:

XI

Accordingly, it is possible that the two bands observed in the region 1724–1695 cm.$^{-1}$ (weak or medium intensity) and 1618–1525 cm.$^{-1}$ are due to the mesoionic structure, XI, although not enough information exists in the literature (15, 16) to firmly support this viewpoint.

The dimethylamino derivative (structure X) exhibits two weak bands at 1441 and 1404 cm.$^{-1}$ (Table II) which when combined result in a medium-intensity band at 1425 cm.$^{-1}$. The methylamino derivative (structure III, R = CH_3) exhibits a prominent shoulder at 1395 cm.$^{-1}$. These bands probably can be ascribed (2, 12) to the N—CH_3 absorption. It is also possible that the band observed in the 1217–1148 cm.$^{-1}$ region (Table II) in all of the derivatives is due to C—N vibration. All of the derivatives exhibit a medium-intensity absorption band between 1297 and 1280 cm.$^{-1}$. The significance of this region will be discussed below. From Table II it can be seen that there are a few characteristic skeletal vibration bands due to the thiatriazole ring itself in the regions 911–889 cm.$^{-1}$, 962–930 cm.$^{-1}$, 1060–1030 cm.$^{-1}$, and 1122–1090 cm.$^{-1}$.

1-Substituted-tetrazolinethiones

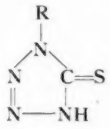
It has recently been found (1) that 5-(substituted)amino-1,2,3,4-thiatriazoles can be partially converted to a tetrazole derivative when the substituent was an aryl group (structure III, R = aryl). The tetrazole derivative produced could be represented in the *thione* (structure IV) or *thiol* (structure V) forms. It was found that structures of the types IV and V could easily be differentiated by a study of their infrared spectra. The results of the present study establish the *thione* (IV) structure for these compounds. Table III summarizes the important bands observed for these derivatives.

In all of the compounds studied, the —N—C=S and C=S bands are strong and are found in the regions 1500–1474 cm.$^{-1}$ and 1359–1338 cm.$^{-1}$, respectively. The more important observation for these series of compounds was the fact that the presence of the SH band in the region 2600–2550 cm.$^{-1}$ (2) was not apparent. This supports the *thione* (IV) structure rather than the *thiol* (V) structure for these compounds.

A few absorption bands are observed in the 1650–1500 cm.$^{-1}$ region. However, no differentiation of the —N=N— linkage is possible. As Ueno (6) and Bellamy (2) point out, the main difficulty is that the —N=N— absorptions are expected to appear in the double-bond region, so that they may well be merged with the conjugated and stronger aromatic ring absorptions. All of the tetrazole derivatives studied (Table III) exhibit two bands of medium intensity around 1210 cm.$^{-1}$ and 1170 cm.$^{-1}$, the former band being very weak in some cases. It is possible that these bands may be due to the C—N linkage. All of the derivatives, including 1-benzyl-tetrazoline-5-thione (IV, R =

TABLE III

INFRARED SPECTRA OF 1-SUBSTITUTED-TETRAZOLINETHIONES



R =	N—C=S	C=S	Cyclic —N—N=N—	Skeletal				
C_6H_5	1498s	1348s	1280s	1096w	1068w	1050m		989m
4-$CH_3C_6H_4$	1500s	1350s	1280s	1115w	1080w	1042s		990m
4-$CH_3OC_6H_4$	1499s	1359m	1302w	1111w		1038s		988m
4-Cl—C_6H_4	1482s	1350s	1280m	1096m	1083m	1046s	1013m	990s
2-$CH_3C_6H_4$	1482s	1352s	1280m			1040m		985m
2-$CH_3OC_6H_4$	1483s	1347s	1280s		1078m	1046s	1018s	985s
$C_6H_5CH_2$	1474s	1338s	1287m	1089m	1075w	1053m	1024w	1000m

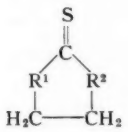
$C_6H_5CH_2$—), show a strong or medium intensity band around 1280 cm.$^{-1}$. The interpretation of this band is discussed below.

All of the observed frequencies in the region 1115–980 cm.$^{-1}$ have been tabulated. Although a few of the weak bands could be due to the substituted aromatic ring, it is also possible that some of the bands are characteristic skeletal vibration bands of the tetrazolinethione system:

In a few cases, only two strong and/or medium-intensity bands at about 1040 and 990 cm.$^{-1}$ are found. If the small peaks in the other compounds are combined into a broad band, two maxima are invariably found at about 1085 and 1040 cm.$^{-1}$, which in addition to the 990 cm.$^{-1}$ band appear to be common to all these compounds. The results are in general agreement with the earlier observations by Lieber (5) for tetrazole derivatives.

The C=S *Frequency*

Bellamy (2) states that no adequate correlation has yet been worked out for this linkage. Colthup (17) and Thompson (18) have suggested the range 1400–1300 cm.$^{-1}$ for the C=S absorption but there is no indication of the classes of compounds on which the assignment is based. Mecke (19) in a recent study ascribed a band of strong intensity in the region 1200–1050 cm.$^{-1}$ for a series of compounds of the type:



where R^1 and R^2 represented the groups CH_2, NH, O, and S, the spectral maps for ethylenethiourea (R^1 = R^2 = NH), oxazolthione (R^1 = NH, R^2 = O), thiopyrrolidone

(R^1 = NH, R^2 = CH_2), thiothiazolidone (R^1 = NH, R^2 = S), and ethylenetrithiocarbonate (R^1 = R^2 = S) being presented in their paper. An examination of these maps reveals bands of strong intensity in the much less variable region of 1350–1300 cm.$^{-1}$. It is more likely that this latter region corresponds to the C=S frequency and that the more variable region of 1200–1050 cm.$^{-1}$ could be assigned to either C—N, C—S, or C—O skeletal vibrations. From the data (Tables I, II, and IV) of the present investigation a frequency assignment of 1395–1338 cm.$^{-1}$ for the C=S linkage can be made.

TABLE IV

IMPORTANT INFRARED FREQUENCY ASSIGNMENTS FOR 4-SUBSTITUTED-THIOSEMICARBAZIDES

$R_1R_2NC(S)NHNH_2$

Frequency, cm.$^{-1}$	Assignment
1555–1488(s)	—N—C=S
1395–1346	C=S
Ref. (4), (5)	—$NHNH_2$ structural
1639–1610(s)	NH_2 deformation, asym.
1280–1259(v)	NH_2 deformation, sym.
1094–1058(v)	NH rocking
996–956(m/s)	NH rocking
815–774(w/m)	NH bending

The —N—C=S *Frequency*

Randall (4) has assigned a strong band to the structure R—N—C=S or R—NH—C=S in the region 1613–1471 cm.$^{-1}$. Mann (20) assigns a band at 1495 cm.$^{-1}$ for this group. Bellamy (2) feels that there is justification for a tentative assignment to the 1500–1470 cm.$^{-1}$ region. From the data of the present investigation on 4-substituted-thiosemicarbazides (Tables I and IV) and on the tetrazolinethiones (Table III) an assignment to the region 1555–1474 cm.$^{-1}$ can be made.

The 1300–1270 cm.$^{-1}$ *Frequency Region*

From Tables II and III it can be seen that the thiatriazole and tetrazolinethione rings exhibit a band in the 1300–1270 cm.$^{-1}$ region* of variable intensity. Since no other assignment seems possible, a tentative assignment of this frequency to the cyclic —N—N=N— linkage is suggested. It is interesting to note that the variable symmetric vibration band of the azido group, N_3, has been assigned the region of 1343–1177 cm.$^{-1}$ by Sheinker and Syrkin (21). Lieber (9) has recently assigned the 1297–1256 cm.$^{-1}$ region to this symmetric vibration band. From the results of Lieber, Levering, and Patterson (5) it can be seen that quite a large number of tetrazole derivatives show this absorption in the 1300–1270 cm.$^{-1}$ region, lending support to a cyclic —N—N=N— assignment.

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**A similar band is exhibited by substituted 1,2,3-triazoles of the configuration:*

These data will be reported in a separate communication.

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RADIOCHEMICAL EVIDENCE FOR HETEROGENEITY IN WHEAT STARCH[1]

A. S. PERLIN

ABSTRACT

Wheat starches labeled with carbon-14 have been fractionated by a novel leaching procedure to give amylose, amylopectin, and a highly-branched minor fraction designated "amylopectin C". Marked differences in the specific activity of the fractions are found. Subfractionation of amylopectin also gives products of varying specific activity. These findings provide radiochemical evidence for heterogeneity in wheat starch.

Starch is composed of D-glucopyranose units joined together, chiefly by 1,4-α-glycosidic linkages, in two distinct macromolecular patterns, one linear and the other highly branched. It is generally accepted that these structural forms are represented in the starch granule by two components, amylose and amylopectin, respectively, which can be isolated and readily differentiated by chemical and physical means (1, 2). In turn, amylose and amylopectin may be subfractionated into products having characteristics substantially different from each other (1, 2, 3, 4, 5, 6), the electrophoretic examination of starch by Lewis and Smith (6) affording particularly striking evidence for such heterogeneity. However, a minority opinion (e.g. 7, 8) holds that starch is homogeneous and that amylose, amylopectin, and subfractions of these are artifacts generated by scission of unstable linkages in an indefinitely large starch molecule. These diverse views on the structure of starch are evaluated critically by Greenwood (2), who concludes that the concept of heterogeneity is favored, a conclusion reached also by Schoch (9), but underlines the difficulty in experimentally proving or disproving such postulates. The current paper provides new evidence for heterogeneity in starch based on differences in the carbon-14 content of amylose, amylopectin, and subfractions of amylopectin, which have been isolated from C^{14}-labeled wheat starches (10).

Amylose and amylopectin are most satisfactorily separated by complete dispersion of the starch in water following which the amylose is preferentially precipitated with a suitable complexing agent (1, 2). The C^{14}-labeled wheat starches were dispersed in water by autoclaving according to the procedure of Schoch (1). It was found, however, that material corresponding to amylopectin (referred to as "amylopectin B") contaminated with very little amylose ("blue values" (11) of 0.1 or less) could be separated out as a gel in a preparative-type ultracentrifuge. Addition of *n*-amyl alcohol to the supernatant solution then precipitated the amylose, which was also of relatively high purity ("blue values" of 1.0 or more). This modification of Schoch's procedure in effect constitutes a leaching process (1, 9) and in its end result resembles the method of Baum, Gilbert, and Wood (12), which employs mild heating in an oxygen-free atmosphere. After removal of the amylose a third starch fraction, referred to as "amylopectin C", was obtained from the solution by flocculation with excess ethanol.

Amylopectin C appears not to have been described by earlier workers. Its yield varied, but averaged about 5% of the total starch. On treatment with iodine the material gave a red color resembling the usual amylopectin–iodine color and, like the major amylopectin fraction ("amylopectin B"), had a "blue value" of 0.1 or less. A comparison of periodate end-group values indicated that the average unit chain lengths of amylopectins B and C

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are of approximately the same order, but an accurate measure was not obtained because the polysaccharides were overoxidized. The apparent degree of hydrolysis of amylopectin C to maltose by β-amylase was 48–53%, somewhat less than the value of 55–60% found for amylopectin B. These properties, together with the fact that the material did not form an insoluble complex with *n*-amyl alcohol, served to characterize the minor starch component as a polymer closely related to amylopectin.

Two samples of amylopectin B were subfractionated, in turn, to give three products each. The first of these was obtained as a flocculus by acidifying an alkaline solution of amylopectin B. High-speed centrifugation of the opaque dispersion remaining yielded a second subfraction as a gel, and a third was precipitated from solution with ethanol. Each of these subfractions was degraded to approximately the same extent (55–60%) by β-amylase.

Marked differences in specific activity were found among the starch fractions and subfractions (Table I), the variations being dependent on the stage of plant growth at which tracer was administered. Amylose thus possessed a lower specific activity than amylopectin B if glucose-1-C^{14} or acetate-C^{14} was fed early, or higher, if a late injection was made. These observed fluctuations are thought to reflect the mode of biosynthesis of the amylose and amylopectin components of wheat starch (13). The specific activity–time pattern of labeling of the amylopectin C fractions was distinct from that of amylopectin B but closely resembled the pattern shown by amylose. Differences were found also among the subfractions of amylopectin B, subfractions 2 and 3 having similar specific activities but subfraction 1 having much higher (early injection) or lower (late injection) specific activity.

TABLE I

SPECIFIC ACTIVITY* OF STARCH FRACTIONS AND SUBFRACTIONS

Tracer:	Glucose-1-C^{14}			Acetate-1-C^{14}		Acetate-2-C^{14}		$C^{14}O_2$
Time given (days†):	67	73	79	70	85	80	85	—
Amylose	104	240	314	47	66	58	56	141
Amylopectin B	196	187	190	60	40	45	33	109
Subfraction 1	339	99						
Subfraction 2	173	215						
Subfraction 3	179	207						
Amylopectin C	116	219	377	46	69	56	65	122

*$m\mu c./mM.$ *carbon dioxide.*
†*Days after seeding.*

These variations in the quantity of carbon-14 incorporated strongly suggest that amylose and amylopectin are deposited in the kernel at far from parallel rates and that the various branched components also are not synthesized simultaneously. Accordingly, wheat starch may be considered heterogeneous in a biosynthetic sense. If starch is a giant homogeneous molecule, and the various materials isolated from it were to represent products of random degradation, differences in the specific activity of these fragments would not be expected. However, the current data do not disagree with the view that starch is an indefinitely large molecule, but require that it be built up in a stepwise manner, the stages being distinguishable by differing chemical characteristics and susceptibilities to degradation. In these terms the concept of heterogeneity in starch is meaningful even if linear and branched components are joined together at certain points within the granule by unstable linkages (7). Alternatively, if amylose and amylopectin

are to be regarded as distinct entities, the present radiochemical evidence indicates that amylopectin is itself heterogeneous and may be fractionated into components which differ in physical properties and, possibly to a lesser extent, in chemical structure.

EXPERIMENTAL

C^{14}-labeled wheat starches were isolated as described earlier (10) from the kernels of mature plants grown under field conditions, a given tracer being administered to the plants at various periods of the growing season (14).

Fractionation of Wheat Starch

The starch (0.2–1.0 g.) was extracted exhaustively with hot methanol (1) and air-dried. It was suspended in water at a concentration of 2% and gelatinized on the steam bath and then autoclaved at 18 lb./sq. in. for 4 hours (1). After cooling, the dispersion was centrifuged in a Spinco preparative ultracentrifuge at 40,000 r.p.m. for 25 minutes, giving a gelatinous sediment. The latter was washed in the centrifuge with water and recovered after dehydration with ethanol and ether (amylopectin B). The combined aqueous supernatant solutions were heated on the steam bath, amyl alcohol (1/10 volume) was added, and the suspension stirred gently and allowed to cool slowly (1). After 18 hours at 3° C., the suspension was centrifuged at 25,000 r.p.m. for 20 minutes, the precipitate was washed in the centrifuge with amyl alcohol-saturated water, then several times with ethanol and ether, and dried (amylose). Methanol (4 volumes) was added to the clear supernatant remaining after separation of amylose, and material which precipitated was recovered and dried after ethanol and ether washes (amylopectin C).

Amylose accounted for 28–33% and amylopectin B for 58–65% of the weight of the starches. The yield of amylopectin C varied widely, ranging in amount from 1 to 15% and averaging about 5% of the starches. Iodine absorption values at 610 mμ ("blue values" (11)), measured for the fractions of four starches by the procedure of McCready and Hassid (15), were as follows: amylose—1.0, 1.1, 1.2, 1.2; amylopectin B—0.08, 0.10, 0.12, 0.16; amylopectin C—0.06, 0.08, 0.10, 0.14. All amylose samples gave the typical intense blue color with iodine, and all amylopectin B and C samples a red-purple color of low intensity.

Subfractionation of Amylopectin B

Amylopectin B (0.5 g.), moistened with ethanol, was pasted in *N* sodium hydroxide (6 ml.). Boiling water (50 ml.) was added, the dispersion cooled, acidified with acetic acid, and centrifuged at 5000 r.p.m. affording a precipitate (subfraction 1). Centrifugation at 40,000 r.p.m. gave a second product as a clear gel (subfraction 2), and addition of methanol (30 ml., 1/2 volume) then yielded a bulky precipitate (subfraction 3). All three materials were recovered by washing with methanol and drying. Two samples of amylopectin B fractionated in this way gave the following percentage yields of subfractions 1, 2, and 3, respectively: 16 and 19, 23 and 21, 51 and 47.

Measurement of β-Amylase Degradation

The amylopectin sample (10 mg.) was pasted in *N* sodium hydroxide (0.2 ml.), then taken up in hot water (1 ml.), and the hydrogen-ion concentration of the cooled solution adjusted to pH 5.0 with acetic acid. An excess of a β-amylase preparation was added and the reaction allowed to proceed at room temperature. Aliquots of the solution were withdrawn at intervals and analyzed for reducing power with the Somogyi reagent (16). Hydrolysis was virtually terminated in 2–3 hours, reducing values being increased by less than 5% during a further 20 hours' reaction time. Chromatographic examination of

the hydrolyzate, after precipitation of limit dextrin with ethanol and removal of sodium ions with Amberlite IR-120, showed maltose as the single sugar produced by β-amylase degradation. The degree of hydrolysis (maltose produced in 5 hours from measure of total reducing power) of four samples of amylopectin B was 55, 58, 59, and 60%, and of four samples of amylopectin C 48, 48, 50, and 53%. Under the same reaction conditions samples of amylose were 90–95% hydrolyzed in 20 hours.

Periodate Oxidation

The starch fraction (15 mg.) was suspended in ethanol (1 ml.), 0.04 *M* sodium metaperiodate (9 ml.) was added, and the mixture stored in the dark at 19.5° C. Aliquots were withdrawn at intervals, excess periodate was destroyed with ethylene glycol, and acid formed was titrated with dilute sodium hydroxide using methyl red indicator. Acid produced (moles/mole) at 75 and 120 hours, respectively, by two samples of amylopectin B: 0.036, 0.041 and 0.052, 0.047; by two samples of amylopectin C: 0.041, 0.039 and 0.053, 0.047.

Measurement of Specific Activity

Specific activity was estimated by the method of Buchanan and Nakao (17). Samples were combusted, and the carbon dioxide liberated was estimated manometrically and its specific activity measured in a gas counter. Reproducibility of the method is ±3%.

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L'ARYLATION DES QUINONES PAR LES SELS DE DIAZONIUM

III. SUR LA SYNTHÈSE DES ARYL-CHLORO-*p*-BENZOQUINONES[1]

P. BRASSARD[2] ET P. L'ÉCUYER

RÉSUMÉ

La chloroquinone réagit avec les sels de benzène- et de *p*-chlorobenzène-diazonium pour donner un mélange de deux isomères monoarylés. La majeure partie du produit de la réaction est l'isomère 2,6 et le reste l'isomère 2,3.

INTRODUCTION

Les phénylbenzoquinones réagissent en solution tampon avec les sels de diazonium (1) pour donner les 2,5-bisphénylquinones correspondantes. Günther (2) a constaté que la chloroquinone réagit aussi avec les sels de diazonium et a même isolé un composé qu'il n'a pas identifié. Était-ce l'isomère 2,5? Il y avait lieu d'en douter; car la chloroquinone et la phénylquinone constituent deux systèmes dans lesquels les effets électromères devraient affecter différemment l'orientation de l'entrée du groupement phényle.

Dans le but d'établir la position du groupe phényle, nous avons effectué la réaction de la chloroquinone avec les chlorures de benzène- et de *p*-chlorobenzène-diazonium dans les mêmes conditions que nous avons établies pour la réaction de la benzoquinone avec ces sels (3), soit en milieu aqueux tamponné par l'acétate de sodium. La purification du produit de la réaction a révélé qu'il se forme dans chaque cas deux isomères au lieu d'une seule substance. Une première cristallisation a permis de les séparer grossièrement. Nous avons ensuite procédé à la purification de chacun d'eux en le cristallisant dans un solvant approprié. Dans les deux cas la purification de l'isomère le moins soluble a été facile, mais celle de l'isomère le plus soluble s'est révélée plus difficile et même impossible dans le cas particulier de l'isomère dans lequel le résidu hydrocarboné est le groupe phényle. Ce dernier composé reste toujours contaminé par une certaine quantité de l'isomère le moins soluble. Pour cette raison nous avons choisi d'identifier d'abord les deux isomères dans lesquels le résidu aryle est le groupe *p*-chlorophényle avant de caractériser l'isomère où le reste aryle est le groupement phényle.

Les analyses indiquaient que nous avions réellement affaire à deux 2-chloro-*x*-(*p*-chlorophényl)-benzoquinones isomères. Or théoriquement, il était possible d'obtenir deux des trois isomères inconnus I, II et III. En l'absence de méthode pour préparer ces derniers de façon non équivoque, la preuve de structure que nous avons établie repose essentiellement sur l'identité des *x*,*x'*-dichloro-*x''*-(*p*-chlorophényl)-benzoquinones obtenues de deux façons différentes. Selon la première, nous avons additionné de l'acide chlorhydrique aux deux 2-chloro-*x*-(*p*-chlorophényl)-benzoquinones isomères, la substance II (Ar = groupe *p*-chlorophényle), p.f. 150°, et la substance I (Ar = groupe *p*-chlorophényle), p.f. 103°, et oxydé ensuite en quinones les hydroquinones que nous avions ainsi obtenues. Selon la deuxième, nous avons fait réagir le chlorure de *p*-chlorobenzène-diazonium avec la 2,3- et la 2,6-dichlorobenzoquinone (V et IV).

La substance II (Ar = groupe *p*-chlorophényle), p.f. 150°, après l'addition de l'acide chlorhydrique et l'oxydation du produit de la réaction au chlorure ferrique, donne un mélange constitué, en majeure partie, de 2,3-dichloro-5-(*p*-chlorophényl)-benzoquinone

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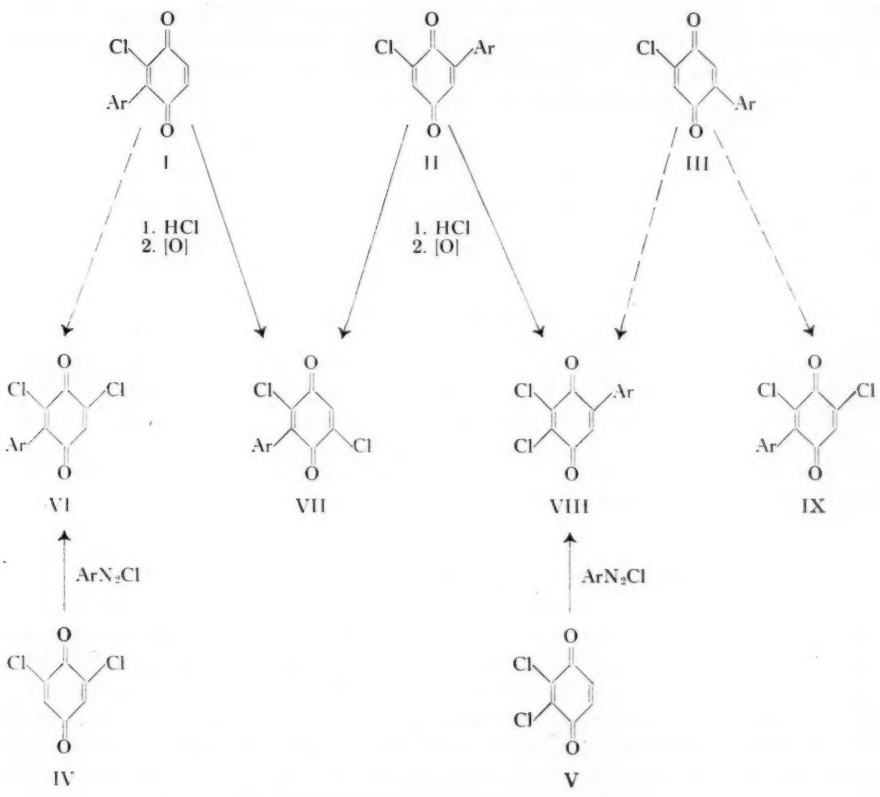


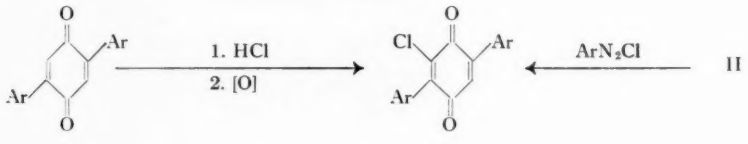
Ar = groupe phényle ou *p*-chlorophényle

(VIII), p.f. 166°–167°, composé que nous avons aussi obtenu par la condensation du chlorure de *p*-chlorobenzène-diazonium avec la 2,3-dichlorobenzoquinone (V), et d'une autre substance, p.f. 144°–145°, différente de l'isomère dichloré en 2,6 (VI), p.f. 116°–117°, et obtenue de IV (Ar = groupe *p*-chlorophényle) par réaction avec le chlorure de *p*-chlorobenzène-diazonium. Cette dernière substance ne peut être que la 2,5-dichloro-3-(*p*-chlorophényl)-benzoquinone (VII), car il ne reste pas d'autre alternative.

L'isomère I (Ar = groupe *p*-chlorophényle), p.f. 103°, soumis à la même série de réactions donne exclusivement une seule substance identique à la 2,5-dichloro-3-(*p*-chlorophényl)-benzoquinone (VII), p.f. 144°–145°, aussi obtenue de l'isomère II, tel que mentionné précédemment. Leur identité a été vérifiée par leur point de fusion mixte. Le fait que celui-ci n'est pas déprimé constitue une preuve rigide que l'isomère II est bien la 2-chloro-6-(*p*-chlorophényl)-benzoquinone et l'isomère I la 2-chloro-3-(*p*-chlorophényl)-benzoquinone.

D'ailleurs, nous avons aussi confirmé ces résultats de la façon suivante. La produit de la réaction de l'isomère II (Ar = groupe phényle), p.f. 128°–129°, avec le chlorure de benzène-diazonium et celui que l'on obtient par l'oxydation de l'hydroquinone résultant de l'addition de l'acide chlorhydrique à la 2,5-bisphénylquinone (X, Ar = groupe

phényle) ne sont qu'une seule et même substance, soit la 3-chloro-2,5-bisphénylbenzoquinone (XI, Ar = groupe phényle). Leur point de fusion est identique et n'est pas déprimé lorsque les deux produits sont mélangés. Donc l'isomère II (Ar = groupe phényle) est bien la 2-chloro-6-phénylbenzoquinone.



Ar = groupe phényle ou *p*-chlorophényle

L'isomère II (Ar = groupe *p*-chlorophényle), p.f. 150°, et la 2,5-bis-*p*-chlorophénylbenzoquinone (X, Ar = groupe *p*-chlorophényle) sont beaucoup plus inertes, mais donnent néanmoins par les mêmes réactions une seule et même substance, la 3-chloro-2,5-bis-*p*-chlorophénylquinone (XI, Ar = groupe *p*-chlorophényle), comme le montre le point de fusion mixte. Donc, c'est là une autre preuve que l'isomère II (Ar = groupe *p*-chlorophényle) est bien la 2-chloro-6-*p*-chlorophénylbenzoquinone.

PARTIE EXPÉRIMENTALE*

2-Chloro-6-phénylbenzoquinone (*II*, Ar = *groupe phényle*)

Une solution de chlorure de benzène-diazonium, préparée par la diazotation de 9.3 g. (0.1 mole) d'aniline dissoute dans 25 ml. d'acide chlorhydrique concentré et 100 ml. d'eau, est versée dans un mélange de 15.7 g. (0.11 mole) de chloroquinone et de 30.6 g. (0.225 mole) d'acétate de sodium trihydraté dans 1300 ml. d'eau. On agite vigoureusement à la température ambiante jusqu'à ce qu'il ne se dégage plus d'azote. On essore le précipité (18.5 g., 84% de la théorie) et on l'extrait à l'éther de pétrole bouillant. Après l'évaporation du solvant on cristallise le résidu dans l'éthanol. Une deuxième cristallisation dans le même solvant donne 11.9 g. (54%) de 2-chloro-6-phénylbenzoquinone pure sous forme de paillettes jaunes, p.f. 127°–129°. Calculé pour $C_{12}H_7O_2Cl$: C, 65.92%; H, 3.21%. Trouvé: C, 85.8%; H, 3.8%. Les eaux-mères de cristallisation contiennent un autre isomère; mais il a été impossible de le débarrasser complètement de l'isomère 2,6 qui est beaucoup moins soluble que lui dans les solvants organiques.

Pour fin d'identification l'isomère 2,6 a été préparé de la façon suivante. On fait barboter de l'acide chlorhydrique gazeux anhydre dans une suspension de 10.0 g. de phénylquinone dans 100 ml. d'acide acétique glacial; la quinone passe lentement en solution au fur et à mesure que celle-ci se sature d'acide chlorhydrique. On refroidit à la température ambiante et on ajoute d'un seul trait 100 ml. d'une solution de chlorure ferrique à 30%. On agite durant quelques secondes et on verse dans un grand volume d'eau. On essore le précipité et on le cristallise dans l'éthanol à 90%. On obtient ainsi 9.7 g. (81%) de 2-chloro-6-phénylbenzoquinone, p.f. 129°–130°. Un mélange en proportions égales de deux échantillons de la quinone obtenue par les deux méthodes différentes fond aussi à 129°–130°.

2,3-Dichloro-5-phénylbenzoquinone (*VIII*, Ar = *groupe phényle*)

En opérant comme précédemment, on additionne à la 2-chloro-6-phénylbenzoquinone (5.0 g.) dans l'acide acétique glacial (75 ml.) de l'acide chlorhydrique anhydre, on oxyde

**Les points de fusion ont été pris à l'aide de l'appareil de Johns.*

à l'aide de 50 ml. d'une solution de chlorure ferrique à 30% et on verse dans 300 ml. d'eau froide. On essore 4.4 g. (76%) de 2,3-dichloro-5-phénylbenzoquinone presque pure. Elle cristallise dans l'acool éthylique en lamelles jaunes, p.f. 166°–167°. Calculé pour $C_{12}H_6O_2Cl_2$: C, 56.95%; H, 2.39%. Trouvé: C, 56.9%; H, 2.5%.

Une solution de chlorure de benzène-diazonium, obtenue par la diazotation de 4.7 g. (0.05 mole) d'aniline dans un mélange de 12.5 ml. d'acide chlorhydrique et de 50 ml. d'eau, est versée dans une solution de 9.7 g. (0.055 mole) de 2,3-dichlorobenzoquinone dans 200 ml. d'acide acétique glacial à la température ambiante. On munit le récipient d'un agitateur mécanique et on y ajoute 15.3 g. d'acétate de sodium trihydraté dissous dans 100 ml. d'eau. Une fois la réaction terminée (environ 12 heures), le produit brut est filtré et bouilli en présence de noir animal dans un mélange de méthanol, d'acétone et d'eau (1:1:1). La solution est filtrée à chaud, refroidie et mise au réfrigérateur. On essore 8.7 g. (69% de la théorie) de 2,3-dichloro-5-phénylbenzoquinone, p.f. 166°–167°. Calculé pour $C_{12}H_6O_2Cl_2$: C, 56.95%; H, 2.39%. Trouvé: C, 57.3%; H, 2.4%. Le mélange d'un échantillon de cette quinone avec un autre de la 2,3-dichloro-5-phénylbenzoquinone obtenue de la façon décrite précédemment fond aussi à 166°–167°.

2-Chloro-6-(p-chlorophényl)-benzoquinone (*II*, Ar = *groupe p-chlorophényle*) *et 2-chloro-3-(p-chlorophényl)-benzoquinone* (*I*, Ar = *groupe p-chlorophényle*)

En condensant, dans les mêmes conditions que pour la synthèse de la 2-chloro-6-phénylquinone, le chlorure de *p*-chlorobenzène-diazonium (0.1 mole) avec la chloroquinone (0.1 mole), on recueille, la réaction terminée, 25.9 g. d'un mélange de deux isomères. On extrait le matériel brut à l'éther de pétrole (p.é. 65°–110°) bouillant et on laisse refroidir les extraits à la température ambiante. Il se sépare d'abord une huile rouge foncé, puis il se dépose des cristaux rouges. Lorsque des aiguilles jaunes commencent à apparaître, on décante la solution (qu'on conserve pour isoler l'autre isomère) et on cristallise le résidu dans l'éthanol. Après quelques cristallisations on obtient 16.0 g. (66% de la théorie) de 2-chloro-6-(*p*-chlorophényl)-benzoquinone pure sous forme d'aiguilles rouges, p.f. 150°. Calculé pour $C_{12}H_6O_2Cl_2$: C, 56.95%; H, 2.39% .Trouvé: C, 56.8%; H, 2.5%.

On évapore à sec la solution dans l'éther de pétrole qu'on a décantée dans la préparation précédente. On dissout ensuite le résidu dans un mélange bouillant de méthanol, d'acétone et d'eau (1:1:1), on traite la solution au noir animal et, après cristallisation, on essore 4.5 g. (18% de la théorie) de 2-chloro-3-(*p*-chlorophenyl)-benzoquinone pure cristallisée en paillettes jaunes, p.f. 103°. Calculé pour $C_{12}H_6O_2Cl_2$: C, 56.95%; H, 2.39%. Trouvé: C, 56.5%; H, 2.5%.

2,3-Dichloro-5-(p-chlorophényl)-benzoquinone (*VIII*, Ar = *groupe p-chlorophényle*) *et 2,5-dichloro-3-(p-chlorophényl)-benzoquinone* (*VII*, Ar = *groupe p-chlorophényle*)

On fait barboter de l'acide chlorhydrique gazeux anhydre dans une suspension de 2-chloro-6-(*p*-chlorophényl)-benzoquinone (2.0 g.) dans l'acide acétique glacial (50 ml.) jusqu'à saturation et, après avoir chassé la majeure partie du gaz chlorhydrique, on oxyde à la température ambiante à l'aide de 50 ml. d'une solution de chlorure ferrique à 30% et on verse dans 300 ml. d'eau froide. Après filtration et cristallisation du précipité dans l'éthanol, on essore 1.4 g. (61%) de 2,3-dichloro-5-(*p*-chlorophényl)-benzoquinone pure sous forme de longues aiguilles rouges, p.f. 166°–167°. Calculé pour $C_{12}H_5O_2Cl_3$: C, 50.12%; H, 1.75%. Trouvé: C, 50.3%; H, 1.9%.

En étendant d'eau les eaux-mères de cristallisation de la 2,3-dichloro-5-(*p*-chlorophényl)-benzoquinone on obtient l'isomère 2,5-dichloro-3-(*p*-chlorophényl)-benzoquinone

qui, après cristallisation dans le méthanol, donne 0.3 g. (14% de la théorie) de la substance pure sous forme d'aiguilles jaunes, p.f. 144°–145°. Calculé pour $C_{12}H_5O_2Cl_3$: C, 50.12%; H, 1.75%. Trouvé: C, 49.9%; H, 1.8%.

Dans le but d'identifier ces deux isomères, le rouge p.f. 166°–167°, et le jaune p.f. 144°–145°, nous avons préparé la 2,3-dichloro-5-(*p*-chlorophényl)-benzoquinone de la façon suivante: la *p*-choraniline (6.4 g., 0.05 mole) dissoute dans un mélange de 12.5 ml. d'acide chlorhydrique concentré et 50 ml. d'eau est diazotée et la solution du sel de diazonium est versée dans un mélange de 9.7 g. (0.055 mole) de 2,3-dichlorobenzoquinone (V) et de 20.4 g. de trihydrate d'acétate de sodium dans 200 ml. d'acide acétique à la température ambiante. Tout en agitant mécaniquement le mélange, on y verse suffisamment d'eau pour produire une légère précipitation de la quinone de départ. Une fois le dégagement gazeux terminé, on filtre et cristallise dans l'éthanol. On essore 11.6 g. (81% de la théorie) de 2,3-dichloro-5-(*p*-chorophényl)-benzoquinone pure sous la forme d'aiguilles rouges, p.f. 166°–167°. Calculé pour $C_{12}H_5O_2Cl_3$: C, 50.12%; H, 1.75%. Trouvé: C, 50.1%; H, 2.0%. Elle est identique à l'isomère rouge obtenu précédemment comme le montre le p.f. 166°–167° de leur mélange.

Une suspension de 2-chloro-3-(*p*-chlorophényl)-benzoquinone (I, Ar = groupe *p*-chlorophényle) (1.5 g.) dans l'acide acétique glacial (20 ml.) est saturée par un courant d'acide chlorhydrique sec et la solution d'hydroquinone obtenue est oxydée par l'addition de 50 ml. d'une solution de chlorure ferrique à 30%. On isole par cristallisation dans l'éthanol 1.2 g. (67% de la théorie) de 2,5-dichloro-3-(*p*-chlorophényl)-benzoquinone pure, p.f. 144°–145°. On ne décèle aucune dépression du point de fusion du mélange de cette substance avec l'isomère jaune, p.f. 144°–145°, obtenu par l'addition d'acide chlorhydrique à la 2-chloro-6-(*p*-chlorophényl)-quinone.

2,6-Dichloro-3-(p-chlorophényl)-benzoquinone (*VI*, Ar = *groupe p-chlorophényle*)

La condensation du chlorure de *p*-chlorobenzène-diazonium (0.1 mole) avec une suspension de 2,6-dichloroquinone (0.1 mole) à la température ambiante dans 300 ml. d'acide acétique en présence du trihydrate d'acétate de sodium (0.225 mole) dure 12 heures. On dilue à l'eau, on décante la liqueur et on extrait le résidu à plusieurs reprises à l'éthanol (80%) bouillant. Les extraits réunis, bouillis avec du noir animal, filtrés à chaud et refroidis donnent 18.1 g. (72% de la théorie) de 2,6-dichloro-3-(*p*-chlorophényl)-benzoquinone pure sous forme de paillettes orangées, p.f. 116°–117°. Calculé pour $C_{12}H_5O_2Cl_3$: C, 50.12%; H, 1.75%. Trouvé: C, 50.3%; H, 2.0%.

3-Chloro-2,5-bisphénylbenzoquinone (*XI*, Ar = *groupe phényle*)

En suivant la technique déjà décrite précédemment, on additionne de l'acide chlorhydrique gazeux à 2.8 g. de 2,5-bisphénylquinone (IX, Ar = groupe phényle) et on oxyde ensuite au chlorure ferrique à 30%. On obtient 2.9 g. (91%) de 3-chloro-2,5-bisphénylbenzoquinone qui cristallise dans l'acide acétique en aiguilles orangées, p.f. 188°–189°. Calculé pour $C_{18}H_{11}O_2Cl$: C, 73.35%; H, 3.76%. Trouvé: C, 73.6%; H, 3.9%.

Cette quinone s'obtient également en faisant réagir une solution de chlorure de benzènediazonium (0.05 mole) avec la 2-chloro-6-phénylbenzoquinone (0.045 mole) dans 300 ml. d'acétone à −5°. Tout en s'assurant d'une forte agitation et du maintien de la température du milieu à moins 0° on ajoute en petites portions de l'acétate de sodium trihydraté (20.4 g. en tout) durant une période de 30 minutes. On laisse ensuite le mélange prendre lentement la température ambiante. La réaction terminée, on étend d'eau, on isole le précipité et on le cristallise dans l'acide acétique. On essore la 3-chloro-2,5-bisphénylbenzoquinone (2.7 g., 20%), p.f. 188°–190°. La technique des points de fusion

mixtes montre que cette substance est identique à celle qui a été obtenue par la méthode précédente.

3-Chloro-2,5-(p-chlorophényl)-benzoquinone (*XI*, Ar = *groupe p-chlorophényle*)

On l'obtient en opérant comme pour la synthèse de la 3-chloro-2,5-bisphénylbenzoquinone par l'addition d'acide chlorhydrique à la 2,5-bis-(*p*-chlorophényl)-benzoquinone suivie de l'oxydation au chlorure ferrique et l'arylation de la 2-chloro-6-(*p*-chlorophényl)-benzoquinone par le chlorure de *p*-chlorobenzène-diazonium. La 3-chloro-2,5-bis-(*p*-chlorophényl)-benzoquinone cristallise dans l'acide acétique en aiguilles orangées de p.f. 205°–207°. Calculé pour $C_{18}H_9O_2Cl_3$: Cl, 32.16%. Trouvé: Cl, 31.9%.

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THE INFRARED SPECTRA OF ORGANO-PHOSPHORUS COMPOUNDS

II. THE 1–2.6 μ REGION[1,2]

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ABSTRACT

The application of near infrared spectra to the study of phosphorus compounds has been investigated. It has been found that each type of radical gives a characteristic set of bands, which are not appreciably affected by changes in the molecule more than two atoms distant. Characteristic group frequencies are given for MeO, EtO, *n*-PrO, *i*-PrO, *n*-BuO, Me, Et, Me_2N, Et_2N, and *i*-Pr_2N groups attached to phosphorus. Only the MeP bands are noticeably altered by the nature of the substitution on the phosphorus atom. Qualitative predictions of the spectra of compounds containing more than one type of C—H group may be made by summing the contributions of the components.

INTRODUCTION

In a previous paper (1) certain features of the infrared spectra of organo-phosphorus compounds were discussed and some new assignments proposed in the 2–26 μ region. In some cases useful information about the environment of the phosphorus atom was obtained by a study of the C—H bending vibrations associated with the ester groups attached to phosphorus. With the advent of commercial spectrophotometers designed to give high resolution in the 0.7–2.5 μ overtone-combination region, it was decided to examine the spectra of organo-phosphorus compounds in this region to determine whether the improved resolution would lead to more information about the environment of hydrogen-containing groups.

EXPERIMENTAL

The preparation of most of the compounds examined has been described elsewhere (2, 3).

A Cary Model 14PM double-beam recording spectrophotometer was used for all spectra. Most spectra were run as approximately 1% w/v solutions in Spectrograde carbon tetrachloride. The path lengths used were 10 cm. and 5 cm. in the 1.0–2.1 μ and 2.1–2.5 μ regions respectively. For the remaining spectra, approximately 0.5% w/v carbon tetrachloride was used in 10-cm. cells over the entire 1.0–2.5 μ region. Bands are cited to the nearest 0.001 μ, and the limits given indicate the maximum variation occurring in the compounds examined. The quoted intensities are 100 times the molar extinction coefficients. The instrumental calibration was checked by comparing the benzene spectrum with that reported by Kaye (4).

RESULTS AND DISCUSSION

Bands in the 1–2.5 μ region arise chiefly from overtones and combination bands involving hydrogen vibrations. Most of the compounds examined show two principal sets of bands at the concentration used: set A, near 1.7 μ, is attributed to the first overtone of the C—H stretching vibrations, with the 4 ν C—H bending vibrations superimposed; set B, located in the 2.2–2.5 μ region, is more intense and is attributed to binary C—H stretching and bending combinations, with lesser contributions from ternary bending

[1]*Manuscript received January 17, 1958.*
Contribution from the Defence Research Chemical Laboratories, Ottawa, Canada. Issued as D.R.C.L. Report No. 234A. Presented in part at the 16th International Conference of the International Union of Pure and Applied Chemistry, Paris, France, July, 1957.
[2]*Reference 1 is considered to be Paper No. I in this series.*

combinations and overtones. In addition, there are corresponding band groups when OH is present which exhibit marked changes as the concentration is altered.

Assignments for various types of hydrogen bands are presented in an excellent review of this field published by Kaye (4). The present work, however, is concerned with the contour of the band envelope associated with larger structural groups in the molecule (e.g. EtO, BuO, $—NMe_2$, etc.). We have found that the bands associated with any one of these groups are remarkably constant, being virtually insensitive to structural changes more than two atoms away, although these changes may affect the C—H fundamentals (1). Despite the variations in the slit widths and the degree of overlapping of bands, useful quantitative data can be obtained from the extinction coefficients associated with various bands in any one type of band envelope.

The various groups examined will be discussed separately. The generalized group frequencies are presented in the text, and most of the detailed examples in the Appendix.

(*a*) MeO *and* MeS *Bands*

Phosphorus compounds containing MeO (Appendix—Table XI) have, in general, two principal bands and several lesser bands in region A. The former occur at $1.680 \pm 0.002\ \mu$ (5952 cm.$^{-1}$) and $1.720 \pm 0.001\ \mu$ (5814 cm.$^{-1}$) with average intensities of 13 and 12 respectively. Similar bands occur in dimethyl carbonate and MeS compounds although MeS bands are more intense. In certain cases the concentration was too low to permit accurate readings for these weak bands, and for the additional weaker bands, one of which occurs at $1.666 \pm 0.017\ \mu$ (6002 cm.$^{-1}$).

The B region contains four principal bands up to $2.5\ \mu$. There appear to be other bands beyond $2.5\ \mu$, in particular one near $2.52\ \mu$, but not all of the compounds were investigated in that region, because of instrumental difficulties. The bands occur at $2.254 \pm 0.002\ \mu$ (4437 cm.$^{-1}$), $2.334 \pm 0.004\ \mu$ (4285 cm.$^{-1}$), $2.387 \pm 0.005\ \mu$ (4189 cm.$^{-1}$), and $2.471 \pm 0.005\ \mu$ (4047 cm.$^{-1}$) with average intensities of 174, 41, 70, and 63 per MeO group respectively. On the basis of intensities MeS seems to have all but the $2.387\ \mu$ band and both MeS-containing compounds have an additional band at $2.319\ \mu$ (4312 cm.$^{-1}$) with an intensity of 164. Dimethyl carbonate has similar bands but methanol has only two.

TABLE I

EtO bands			EtS bands		
Band position		$\epsilon \times 10^2$ per EtO group	Band position		$\epsilon \times 10^2$ per EtO group
μ	cm.$^{-1}$		μ	cm.$^{-1}$	
A region					
1.682±0.003	5945	21	1.687	5928	26
1.692±0.003	5910	26	1.695	5859	26
1.727±0.007	5790 br*	23	1.740	5757	42
1.760±0.004	5682	15			
B region					
2.262±0.007	4425	169	2.268	4409	133
2.302±0.004	4344	131	2.284	4378	121
2.342±0.006	4270	78	2.304	4340	172
2.410±0.004	4149	74	2.362	4234	101
2.453±0.005	4077	89	2.397	4172	70
2.482±0.005	4029	83	2.432	4112	26
			2.453	4077	42
			2.484	4026	51
			2.502	3997	43
			2.512	3981	50

**In this and subsequent tables*—sh = *shoulder*, wk = *weak*, br = *broad*, d = *doublet*.

(*b*) EtO *and* EtS *Bands*

Organo-phosphorus compounds whose only C—H bands are contained in ethoxy groups have four bands in the A region and six bands in the B region listed in Table I.

The ethylthio group frequencies, also given in Table I, are based on SSS-triethyl phosphorotrithioate only.

The bands of the compounds on which these characteristic frequencies are based are listed in the Appendix (Table XII), along with the bands for ethanol, ethanethiol, diethyl carbonate, and diethyl oxalate. The EtO compounds without phosphorus have spectra generally similar to the EtO—P compounds. Diethyl oxalate, in particular, has a spectrum almost indistinguishable from those of EtO—P containing compounds.

(*c*) *n*-PrO *Bands*

n-PrO—P compounds have three bands in the A region and nine bands in the B region, the frequencies for which are listed in Table II.

TABLE II

n-PrO bands			*i*-PrO bands			*n*-BuO bands		
Band position		$\epsilon \times 10^2$ per *n*-PrO group	Band position		$\epsilon \times 10^2$ per *i*-PrO group	Band position		$\epsilon \times 10^2$ per BuO group
μ	cm.$^{-1}$		μ	cm.$^{-1}$		μ	cm.$^{-1}$	
A region								
1.698±0.001	5889	27	1.682±0.003	5945	28	1.693±0.003 sh	5907	24
1.730±0.001	5780	27	1.692±0.004	5906	37	1.703±0.001	5872	34
1.754±0.001	5701	21	1.731±0.002	5777	26	1.714±0.002	5834	31
			1.756±0.011 br	5695	14	1.732±0.005	5770	29
			1.800±0.002	5555	11	1.750±0.003	5712	28
B region								
2.269±0.004	4407	157	2.266±0.002	4413	149	2.270±0.009	4405	160
2.300±0.003	4349	153	2.295±0.005	4357	167	2.304±0.003	4340	178
2.313±0.002	4323	135	2.322±0.004	4307	172	2.348±0.002	4259	128
2.348±0.001	4259	103	2.343±0.003	4268	99	2.386±0.002	4191	116
2.366±0.003	4239	91	2.404±0.005	4160	121	2.436±0.003	4105	115
2.388±0.001	4188	80	2.432±0.005	4112	125	2.452±0.002	4078	127
2.426±0.005	4122	92	2.455±0.007	4074	116	2.485±0.003	4024	102
2.447	4087	100	2.475±0.003	4040	95	2.504±0.001	3994	94
2.487±0.001	4021	93	2.518±0.008	3971	61			
			2.551±0.007	3920	51			
			2.587±0.007	3865	49			

(*d*) *i*-PrO *Bands*

i-PrO bands have five bands in the A region and eleven bands in the B region as shown in Table II.

Isopropyl alcohol has similar bands in the A region, shifted slightly to lower frequencies, but the B region is quite different, as there are only four main bands, with numerous shoulders not recorded in the table. Isopropyl frequencies and intensities are not as constant as those due to *n*-propyl.

(*e*) *n*-BuO *Bands*

The characteristic frequencies are also listed in Table II. It is noted from the examples in the Appendix that the intensities of the bands in the B region are in general greater for compounds containing P→S than for those with P→O.

(*f*) MeP *and* MeI *Bands*

Three compounds were examined which contained only Me—P groups. These are listed in Table III along with methyl iodide. Because of the differences among MeI,

Me—P(O), and Me—P(S) type compounds, separate values are given for each class. It is interesting to note that MeI and Me—P compounds show greater dissimilarity in the 1–2.6 μ region than in the 3–16 μ region.

TABLE III

MeP AND MeI BANDS

$MePCl_2$			$MeP(O)Cl_2$			$MeP(S)Cl_2$			MeI		
μ	cm.$^{-1}$	$\epsilon\times10^2$	μ	cm.$^{-1}$	$\epsilon\times10^2$	μ	cm.$^{-1}$	$\epsilon\times10^2$	μ	cm.$^{-1}$	$\epsilon\times10^2$
A region											
1.680	5952	22	1.668	5995	19	1.670	5988	23	1.641	6094	12
1.694	5903	28	1.684	5938	40	1.686	5931	51	1.658	6031	60
1.721	5811	20	1.710	5848	21	1.717	5824	40	1.692	5910	25
1.738	5754	9	1.717	5824	25	1.730	5780	51	1.708	5855	51
1.755	5698	7	1.728	5787	26						
1.762	5675	8									
1.770	5650	7									
1.811	5522	4									
B region											
2.282	4382	134	2.277	4392	202	2.279	4388	272	2.242	4460	194
2.287	4373	137	2.312	4325	59	2.336	4281	111	2.334	4284	111
2.322	4307	21	2.339	4269	67	2.561	3905	149	2.547	3926	122
2.344	4266	113	2.566	3897	114	2.617	3821	156			
2.354	4248	82	2.629	3804	119	2.630	3802	133			
2.379	4203	13									
2.389	4186	17									
2.458	4068	33									
2.536	3943	17									
2.567	3896	20									
2.587 sh	3865	36									
2.593	3857	39									

(*g*) EtP *and* EtI *Bands*

$EtP(O)Cl_2$ and EtI had bands as listed in Table IV. As with the methyl homologues, the near infrared spectrum of EtI differs considerably from that of $EtP(O)Cl_2$.

TABLE IV

$EtP(O)Cl_2$			EtI		
μ	cm.$^{-1}$	$\epsilon\times10^2$	μ	cm.$^{-1}$	$\epsilon\times10^2$
A region					
1.651	6057	11	1.671	6984	15
1.678	5959	14	1.701	5879	36
1.688	5924	22	1.724	5800	36
1.699	5886	wk	1.748	5721	12
1.708	5855	14	1.776	5631	9
1.712	5841	14			
1.731	5777	31			
1.742	5746	41			
1.763	5672	23			
B region					
2.255	4435	112	2.266	4413	200
2.292	4363	124	2.300	4348	153
2.304	4340	131	2.330	4292	73
2.372	4216	90	2.361	4235	148
2.399	4168	53	2.386	4191	151
2.437	4103	32	2.454	4075	89
2.531	3951	76	2.504	3994	75
2.552	3918	76	2.513	3979	49

(*h*) Me_2N *Compounds*

Two compounds containing Me_2N—P and one containing Me_2N—C(O) were examined. These all are quite similar in the A region and the Me_2N—P compounds are similar in the B region. The assigned intensities listed in Table V are for the complete Me_2N grouping.

TABLE V

Me_2N GROUPS

$Me_2NP(S)Cl_2$			$Me_2NP(O)Cl_2$			$Me_2NC(O)H$			Average assignments		
μ	cm.$^{-1}$	$\epsilon\times10^2$	μ	cm.$^{-1}$	$\epsilon\times10^2$	μ	cm.$^{-1}$	$\epsilon\times10^2$	μ	cm.$^{-1}$	$\epsilon\times10^2$
A region											
1.683	5942	12	1.682	5945	15	1.684 sh	5938	20	1.683	5942	14
1.699	5886	26	1.699	5886	29	1.704	5869	39	1.699	5886	28
1.729	5784	17	1.728	5787	19	1.739	5750	27	1.729	5784	18
1.749	5718	12	1.749	5718	15				1.749	5718	14
B region											
2.254	4437	103	2.247 sh	4450	120				2.251	4442	112
2.269	4407	183	2.269	4407	200	2.282	4382	291	2.269	4409	192
2.290	4367	116	2.287	4373	149	2.302	4344	291	2.289	4369	133
2.329	4294	63	2.351	4254	108	2.348	4259	131	2.354	4248	95
2.357	4243	82				2.364	4230	134	2.454	4075	77
2.455	4073	71	2.452	4078	83	2.388	4188	114	2.502	3997	76
2.503	3995	63	2.500	4000	88	2.456	4072	139			
						2.492	4013	94			
						2.534	3946	87			

(*i*) Et_2N *Compounds*

Bands given by Et_2NPSCl_2 are compared with those from Et_3N in Table VI. Intensities given are per Et group.

TABLE VI

Et_2N GROUPS

Et_2NPSCl_2			Et_3N		
μ	cm.$^{-1}$	$\epsilon\times10^2$	μ	cm.$^{-1}$	$\epsilon\times10^2$
A region					
1.683	5942	19	1.687	5928	25
1.693	5907	23	1.697	5893	28
1.732	5774	19	1.737	5757	31
1.761	5679	12	1.766 sh	5663	20
B region					
2.266	4413	121	2.267	4411	99
2.307	4335	116	2.310	4329	141
2.337	4279	66	2.346	4263	75
2.388	4188	62	2.401	4165	85
2.414	4143	55	2.472	4045	73
2.456	4072	63			
2.476	4039	67			
2.492	4013	54			

(*j*) *i*-Pr_2N *Compounds*

Four compounds were examined which contained *i*-Pr_2N in conjunction with other alkoxy groups. A pure sample of a compound containing C—H in *i*-Pr_2N groups only has

not yet been obtained. An attempt was made to predict the spectrum of such a compound by subtracting the contributions of the alkoxy groups. The results are indicated in Table VII. The bands for these compounds are given in Appendix Table XV. Because of the similarity of *i*-PrO and *i*-Pr_2N bands the values in column 3 are probably most reliable.

TABLE VII

PREDICTED *i*-Pr_2N BANDS, μ ($\epsilon \times 10^2$), FOR FOUR COMPOUNDS

i-$Pr_2NP(S)(OEt)_2$	*i*-PrNP(S)(O *n*-Pr)$_2$	*i*-$Pr_2NP(S)(O$ *i*-Pr)$_2$	*i*-$Pr_2NP(S)(O$ *n*-Bu)$_2$
1.687 (56)	1.689 (90)	1.688 (46)	1.690 (37)
1.698 (58)	1.699 (69)	1.697 (46)	1.699 (36)
1.735 (58)	1.721 (26)	1.734 (48)	1.721 (26)
1.764 (28)	1.736 (47)	1.764 (33)	1.737 (37)
1.807 (29)	1.758 (34)	1.806 (16)	1.759 (29)
	1.808 (37)		1.808 (38)
2.267 (181)	2.276 (221)	2.268 (200)	2.274 (162)
2.303 (284)	2.303 (268)	2.302 (372)	2.304 (288)
2.342 (120)	2.346 (134)	2.341 (150)	2.340 (108)
2.360 (280)	2.388 (204)	2.362 (276)	2.399 (129)
2.406 (154)	2.401 (148)	2.404 (183)	2.405 (368)
2.447 (102)	2.447 (140)	2.434 (122)	2.466 (153)
2.467 (286)	2.462 ? (142)	2.462 (136)	2.545 (182)
2.482 br, sh (68)			

(*k*) *Miscellaneous*

Although the P—H group does not give rise to any sharp bands in this region, a weak diffuse band appears at about 1.892 ± 0.001 (5258 cm.$^{-1}$), with an intensity of 24 as indicated in Table VIII.

TABLE VIII

P—H VIBRATIONS

Compound	μ	cm.$^{-1}$	$\epsilon \times 10^2$
Dimethyl hydrogen phosphonate	1.892	5285	26
Diethyl hydrogen phosphonate	1.891	5288	20
Diethyl hydrogen phosphonothioate	1.893	5283	25
Dibutyl hydrogen phosphonate	1.891	5288	23

The P—SH grouping is mainly unbonded at the concentrations used and gives rise to a weak doublet at 1.970 μ (5076 cm.$^{-1}$) and 1.999 μ (5002 cm.$^{-1}$) with intensities of 19 and 19 as indicated in Table X. In contrast, diethylaminoethanethiol and ethanethiol have a band near 1.740 μ (5747 cm.$^{-1}$) in the C—H A region which might be attributed to the S—H group. Phosphorothioic acids, which appear from the 3–15 μ region to have the P(S)OH structure, have a band at 1.908 μ (5241 cm.$^{-1}$) which may arise from the P—OH grouping.

Diethyl phosphoroamidate had NH overtones at 1.481 μ (6739 cm.$^{-1}$) and 1.488 μ (6720 cm.$^{-1}$) and a combination band at 1.992 μ (5020 cm.$^{-1}$) with intensities of 50, 56, and 197 respectively whereas C—NH bands absorb at 1.531 μ (6532 cm.$^{-1}$) and 1.548 μ (6460 cm.$^{-1}$) with intensities of 72 and 73 in isopropylamine and diisopropylamine respectively. There are numerous weak combination bands in these aliphatic amines, none with intensities over 55.

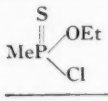
TABLE IX—PREDICTIONS

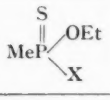
A. 2EtO, 1EtS

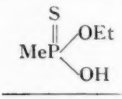
$(EtO)_2P(O)SEt$	Predicted	$(EtO)_2P(S)SEt$
μ ($\epsilon\times10^2$)	μ ($\epsilon\times10^2$)	μ ($\epsilon\times10^2$)
1.685 (64)	1.685 (68)	1.687 (60)
1.691 (72)	1.694 (78)	1.693 (77)
1.732 (79)	1.735 (88)	1.732 (87)
1.761 (39)	1.760 (30)	1.762 (42)
2.263 (429)	2.265 (471)	2.263 (444)
	2.284 (121)	
2.302 (383)	2.302 (434)	2.305 (413)
2.345 (175)	2.342 (156)	2.344 sh (196)
2.359 (197)	2.362 (101)	2.360 (206)
2.398 sh (150)	2.397 (70)	2.397 (157)
2.411 (169)	2.410 (148)	2.412 (167)
2.453 (210)	2.453 (220)	2.452 (212)
2.483 (212)	2.483 (217)	2.482 (200)

B. MeP Compounds*

$MeP(OEt)_2$		$MeP(O)(OEt)_2$		$MeP(S)(OEt)_2$	
Predicted	Observed	Predicted	Observed	Predicted	Observed
1.681 (64)	1.681 (52)	1.668 (19)	1.672 sh (26)	1.670 (23)	1.673 (28)
1.693 (84)	1.694 (63)	1.683 (82)	1.682 (69)	1.684 (93)	1.683 (75)
1.721 (20)	1.716 sh (39)	1.692 (52)	1.692 (55)	1.692 (52)	1.692 (58)
1.727 (46)	1.727 (54)	1.714 (46)	1.714 sh (47)	1.717 (40)	1.717 sh (49)
1.739 (54)	1.736 (58)	1.728 (72)	1.728 (72)	1.728 (97)	1.728 (83)
1.758 (45)	1.757 (30)	1.760 (30)	1.759 (32)	1.760 (30)	1.760 (35)
2.262 (338)	2.269 (321)	2.270 (540)	2.271 (534)	2.271 (610)	2.271 (461)
2.285 (271)	2.280 (359)	2.303 (262)	2.304 (294)	2.303 (262)	2.302 (302)
2.303 (262)	2.305 (324)	2.312 (59)	2.324 sh (183)	2.339 (267)	2.331 (212)
2.322 (21)	2.351 (253)	2.340 (223)	2.340 (170)	2.410 (148)	2.403 (154)
2.343 (269)	2.388 wk (113)	2.410 (148)	2.411 (164)	2.453 (178)	2.452 (191)
2.354 (82)	2.403 (153)	2.453 (178)	2.458 (213)	2.482 (166)	2.482 (176)
2.384 (30)	2.453 (198)	2.482 (166)	2.482 (200)	2.561 (149)	2.565 (156)
2.400 (165)	2.482 (188)	2.566 (114)	2.571 (167)	2.617 (156)	2.617 (172)
2.456 (211)		2.629 (119)	2.619 (193)		
2.482 (166)					







Observed	Predicted	Observed	$MeP(S)(O\ i\text{-}Pr)_2$	
			Predicted	Observed
1.669 (20)	1.670 (23)	1.671 sh (20)	1.670 (23)	1.672 sh (26)
1.682 (59)	1.684 (61)	1.683 (42)	1.684 (107)	1.683 (78)
1.689 (25)	1.692 (26)	1.691 sh (28)	1.692 (74)	1.692 (66)
1.716 (43)	1.717 (40)	1.717 (32)	1.717 (40)	1.719 sh (40)
1.729 (58)	1.729 (74)	1.729 (47)	1.731 (103)	1.730 (76)
1.761 (14)	1.760 (15)	1.759 (26)	1.756 (28)	1.758 (32)
			1.800 (22)	1.801 (27)
2.261 (212)	2.262 (169)	2.262 (159)		
2.275 (348)	2.279 (272)	2.273 (241)	2.273 (580)	2.272 (380)
2.301 (151)	2.303 (131)	2.301 (127)	2.295 (334)	2.297 (312)
2.337 (157)	2.336 (111)	2.327 (124)	2.322 (344)	2.322 (348)
2.412 (79)	2.342 (78)	2.411 (84)	2.340 (309)	2.388sh (235)
2.449 (115)	2.410 (74)	2.450 (94)	2.404 (242)	2.406 (222)
2.481 (101)	2.453 (89)	2.479 (94)	2.432 (250)	2.433 (247)
2.556 (143)	2.482 (83)	2.567 (115)	2.455 (232)	2.450sh (215)
2.612 (156)	2.561 (149)	2.617 (122)	2.475 (190)	2.472 (181)
2.627 (196)	2.617 (156)	2.634 (120)	2.518 (122)	2.518 (137)
	2.630 (133)		2.551 (102)	2.560 (167)
			2.561 (149)	2.613 (175)
			2.617 (156)	2.628 (170)
			2.630 (133)	

Owing to the marked differences among MeP=, MeP(S)=, and MeP(O)= band positions, separate predictions were made depending on the nature of the Me—P group.

TABLE IX (*concluded*)

C. Et—P and R_2N Compounds

$(EtO)_2P(O)Et$		$Me_2NP(O)(OEt)_2$	$Me_2N(OEt)_2$	$Me_2NP(S)(OEt)_2$
Predicted	Observed	Observed	Predicted	Observed
1.651 (11)		1.682 (53)	1.683 (56)	1.683 (55)
1.680 (56)	1.681 (52)	1.692 (70)	1.695 (80)	1.693 (72)
1.690 (74)	1.692 (69)	1.730 (67)	1.728 (64)	1.731 (69)
1.710 (28)	1.715 (30)		1.749 (14)	
1.729 (77)	1.731 (68)	1.761 (41)	1.760 (30)	1.761 (42)
1.742 (41)				
1.762 (53)	1.755 (49)	2.261 (448)	2.257 (450)	2.264sh (475)
2.259 (450)	2.260 (394)	2.267 sh (430)	2.269 (192)	2.270 (507)
2.292 (124)	2.304 (372)	2.302 (417)	2.296 (395)	2.302 (459)
2.304 (393)	2.342 (175)	2.346 sh (230)	2.342 (156)	2.347 (243)
2.342 (156)	2.371 (150)	2.356 (263)	2.354 (95)	2.360 (259)
2.372 (90)	2.416 (162)	2.383 (173)	2.410 (148)	2.387 (183)
2.405 (201)	2.450 (181)	2.410 (202)	2.454 (255)	2.412 (214)
2.437 (32)	2.483 (187)	2.457 (253)	2.482 (166)	2.453 (282)
2.453 (178)		2.480 (241)	2.502 (76)	2.480 (251)
2.482 (166)		2.498 (241)		2.501 (234)

$Me_2NP(O)(OEt)Cl$	Me_2N,OEt	$Me_2NP(S)(OEt)Cl$	$Et_2NP(S)(OEt)_2$	
Observed	Predicted	Observed	Predicted	Observed
1.681 (35)	1.683 (35)	1.682 (37)	1.683 (80)	1.688 sh (70)
1.692 (44)	1.695 (54)	1.692 (47)	1.693 (98)	1.696 (92)
1.703 (38)	1.728 (41)	1.706 (43)	1.730 (84)	1.732 (72)
1.727 (46)	1.754 (29)	1.728 (46)	1.761 (54)	1.763 (49)
1.755 (25)		1.757 (29)		
2.261 (282)	2.251 (412)	2.261 sh (340)	2.264 (580)	2.267 (531)
2.300 (233)	2.266 (361)	2.269 (363)	2.305 (494)	2.307 (532)
2.347 sh (118)	2.296 (264)	2.297 (276)	2.340 (288)	2.340 (285)
2.352 (170)	2.342 (78)	2.340 sh (150)	2.388 (124)	2.391 (209)
2.371 (106)	2.354 (75)	2.354 (189)	2.412 (258)	2.411 (230)
2.409 (115)	2.410 (74)	2.385 (117)	2.455 (304)	2.452 (290)
2.453 (154)	2.454 (166)	2.410 (130)	2.479 (300)	2.480 (298)
2.482 (157)	2.482 (83)	2.452 (179)	2.492 (108)	
2.496 (154)	2.502 (76)	2.482 (165)		
		2.498 (155)		

$Et_2NP(S)(O\,n\text{-}Pr)_2$		$Et_2NP(S)(O\,i\text{-}Pr)_2$		$Et_2NP(S)(OBu)_2$	
Predicted	Observed	Predicted	Observed	Predicted	Observed
1.683 (38)	1.688 sh (70)	1.683 (94)	1.683 (86)	1.683 (38)	1.688 (70)
1.696 (100)	1.698 (96)	1.693 (120)	1.696 (116)	1.693 (94)	1.702 (97)
1.731 (92)	1.732 (82)	1.732 (90)	1.732 (83)	1.703 (68)	1.720 (83)
1.758 (56)	1.756 (60)	1.759 (52)	1.762 (50)	1.714 (62)	1.736 (84)
		1.800 (22)	1.803 (39)	1.732 (96)	1.756 sh (75)
				1.756 (80)	
2.268 (556)	2.274 br (544)	2.266 (540)	2.268 (514)	2.268 (562)	2.272 (559)
2.304 (538)	2.306 br (543)	2.295 (234)	2.295 sh	2.306 (558)	2.307 (629)
2.313 (270)	2.348 (318)	2.307 (232) 910	2. 307 (581)	2.337 (132)	2.336 (386)
2.342 (338)	2.366 sh (265)	2.322 (344)	2.318 sh	2.348 (256)	2.350 (371)
2.366 (182)	2.391 (194)	2.337 (132)	2.340 sh (355)	2.387 (356)	2.387 (374)
2.388 (124)	2.422 (294)	2.340 (330)	2.405 (348)	2.414 (110)	2.414 sh (300)
2.420 (294)	2.452 (306)	2.409 (352)	2.435 (252)	2.436 (230)	2.438 (323)
2.452 (326)	2.486 (304)	2.432 (250)	2.458 (317)	2.454 (380)	2.452 (374)
2.476 (136)		2.476 (324)	2.471 (338)	2.476 (134)	2.473 (42)
2.489 (294)		2.492 (108)	2.492 sh (210)	2.485 (204)	2.483 (330)
		2.518 (122)	2.517 (201)		
		2.551 (102)	2.561 (161)		
		2.587 (98)	2.588 (140)		

TABLE X

P—SH AND P—OH VIBRATIONS

Compound	P—SH			P—OH		
	μ	cm.$^{-1}$	$\epsilon \times 10^2$	μ	cm.$^{-1}$	$\epsilon \times 10^2$
Dimethyl phosphorodithioic acid	1.970	5076	13	2.000	5000	13
Diethyl phosphorodithioic acid	1.969	5079	24	1.998	5005	24
Di-*n*-propyl phosphorodithioic acid	1.972	5071	23	2.001	4998	21
Di-isopropyl phosphorodithioic acid	1.969	5079	23	1.998	5005	23
Di-*n*-butyl phosphorodithioic acid	1.970	5076	13	2.000	5000	13
Diethylaminoethanethiol	1.738	5754	62			
Ethanethiol	1.741	5744	65			
Ethyl methylphosphonothioic acid	1.906	5247	26			
Diethyl phosphorothioic acid	1.909	5238	49			

APPLICATION

A larger number of compounds have been examined which have C—H present in more than one type of group. Spectra have been predicted for these compounds and in Table IX the observed spectra are compared with the predicted spectra. For example, the spectrum of diethyl methylphosphonate is predicted by summing the band positions and intensities for one Me—P(O) and two EtO—P groups. Where bands occur within 0.005 μ in both types of group, or at greater separations in the case of broad bands, one band is predicted at intermediate values with intensity equal to the sum of both contributing groups.

It will be apparent that spectra of compounds with more than one type of C—H containing group cannot be predicted as accurately as those with only one such group. In particular, it is difficult to know when to average positions for bands of neighboring frequencies. Sometimes an average frequency band appears with intensities close to the summed value, and sometimes shoulders appear on the main band with intensities greater than would be predicted owing to the intensity contribution of the larger band. Bands which are weak in the parent compound may be absent or may appear as weak shoulders on the side of a larger band with consequently greater than predicted intensity. It is surprising that the agreement is as good as it is considering that the original intensity assignments are based on peak heights on a band contour, without analysis of the curves. Agreement in the B region is not so good, probably because of the greater complexity, and therefore greater interference from neighboring groups.

The same type of prediction can be made instrumentally. If it is desired to know the spectrum of a compound R′R″R‴P(X), where R′, R″, and R‴ are hydrogen-containing groups, equimolar quantities of R′P(X)Y_2, R″P(X)Y_2, and R‴P(X)Y_2, where Y is any group not containing hydrogen, are placed in series in the spectrophotometer and the addition spectrum is recorded. Three examples of this type of prediction are shown in Fig. 1. The intensities on the graphs are not directly comparable as different concentrations were used in the two cases. The extinction coefficients calculated from the curves show agreement of the same order with those calculated by addition of the extinction coefficients of the component curves.

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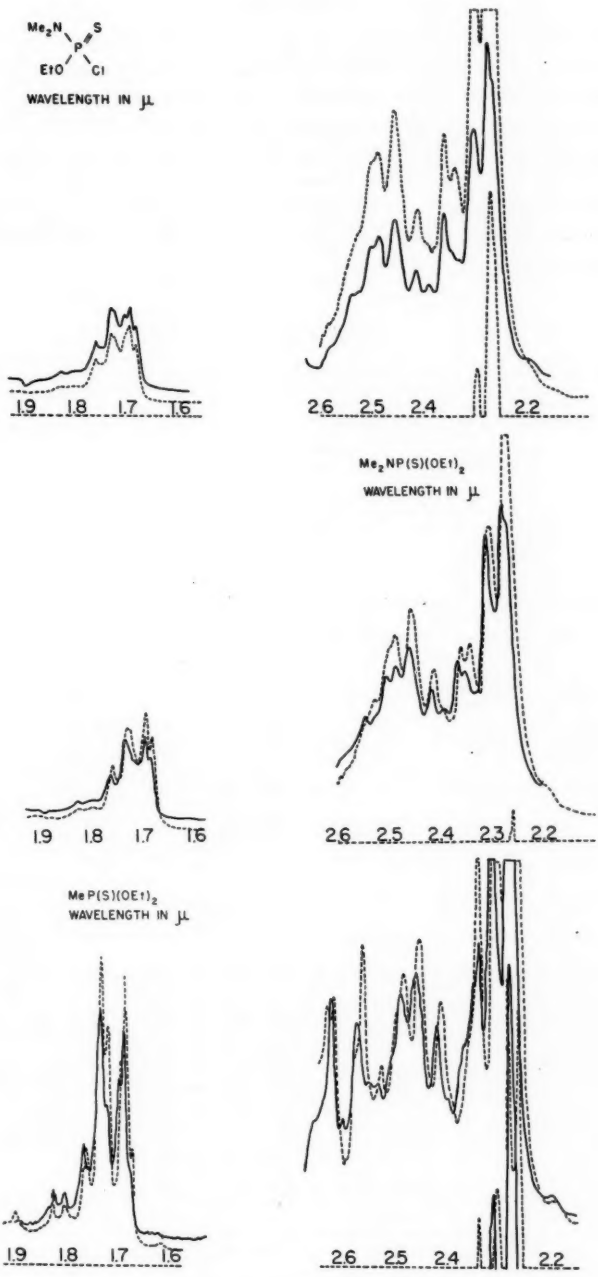

FIG. 1. Observed spectrum, ————————. Spectrum obtained by addition, - - - - - - - - -.

RÉSUMÉ

On a étudié les spectres infrarouges de quelques composés phosphorés dans la région 1.0–2.6 μ. Chaque radical donne plusieurs bandes charactéristiques qui sont presque indépendants des altérations de la molécule à des distances supérieures à deux atomes. On propose des fréquences charactéristiques pour les groupements MeO, EtO, *n*-PrO, *i*-PrO, *n*-BuO, Me, Et, Me_2N, Et_2N, et *i*-Pr_2N reliés directement au phosphore. Les autres substituants de l'atome de phosphore n'affectent que les bandes attribuées au groupement Me—P. D'ailleurs, on peut prédire qualitativement l'allure des spectres des composés contenant plus qu'un type de groupement C—H, en additionnant les fréquences et les intensités des groupes composants.

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APPENDIX

TABLE XI

MeO and MeS* groups

Compounds	Band positions in μ ($\epsilon \times 10^2$)			
A region				
OOS-Trimethyl phosphorothioate	1.666 (12^3)†	1.679 (26+30)†	1.720 (24+31)	
OOS-Trimethyl phosphorodithioate	1.670 (10^3)	1.681 (26+44)	1.723 (24+43)	
Trimethyl phosphorothionate	1.670 (14)	1.680 (16)	1.720 (15)	
Dimethyl phosphorodithioic acid	1.668 (10)	1.681 (13)	1.719 (11)	
Trimethyl phosphate	1.667 (8)	1.681 (10)	1.719 (9)	
Dimethyl hydrogen phosphonothionate	1.669 sh? (10)	1.680 (12)	1.721 (11)	
Dimethyl hydrogen phosphate	1.649 (15)	1.678 (13)	1.72 br (12)	
Dimethyl carbonate	1.651 (12)	1.678 (15)	1.718 (12)	
Methanol	1.664 (8)	1.69 sh (11)	1.702 (14)	

	MeO				MeS
B region					
Dimethyl hydrogen phosphonothioate	2.256 (175)	2.338 (39)	2.392 (71)	2.478 (54)	
OOS-Trimethyl phosphorothioate	2.255 (178^3)	2.332 (40^3)	2.384 (75^2)	2.466 (55^2)	2.319 (153)
OOS-Trimethyl phosphorodithioate	2.253 (180^3)	2.337 (42^3)	2.390 (81^2)	2.475 (50^3)	2.319 (174)
Trimethyl phosphorothionate	2.253 (181)	2.332 (46)	2.385 (75)	2.470 (75)	
Dimethyl phosphorodithioic acid	2.253 (185)	2.336 (38)	2.387 (65)	2.470 (57)	
Trimethyl phosphate	2.253 (158)	2.332 (43)	2.385 (58)	2.466 (73)	
Dimethyl hydrogen phosphonate	2.252 (161)	2.330 (53)	2.386 (64)	2.472 (74)	
Dimethyl carbonate	2.252 (220)	2.336 (72)	2.362 (54) 2.374 (55)	2.452 (51)	2.403 (54)‡ 2.429 (42)
Methanol	2.280 (137)	2.342 (70)	2.522 (108)		

**In this and subsequent tables*—sh = *shoulder*, wk = *weak*, br = *broad*, d = *doublet*.

†12^3 *indicates the observed intensity was divided by 3, i.e. that it is assumed that all substituent groups are contributing to the band. Intensities expressed by a sum indicate an effort to assess the contributions of the* SMe *and* OMe *separately.*

‡*These unassigned bands of dimethyl carbonate are included for completeness.*

TABLE XII

EtO AND EtS

Compound	Band positions in μ ($\epsilon \times 10^2$)					
A region						
Triethyl phosphite	1.683 (18)	1.693 (22)	1.722 (20)	1.760 (12)		
Triethyl phosphorothionate	1.682 (21)	1.692 (27)	1.728 (23)	1.758 (15)		
Triethyl phosphate	1.682 (15)	1.691 (18)	1.727 (15)	1.758 (10)		
Diethyl hydrogen phosphonate	1.682 (21)	1.692 (25)	1.723 (22)	1.761 (14)		
Ethyl phosphorodichloridothionate	1.682 (24)	1.691 (27)	1.721 (27)	1.756 (15)		
Diethyl phosphoroamidate	1.683 sh (20)	1.693 (26)	1.728 (23)	1.762 (16)		
Diethyl hydrogen phosphonothionate	1.683 (20)	1.692 (26)	1.727 (23)	1.762 (15)		
Diethyl phosphorochloridothionate	1.680 (22)	1.689 (30)	1.726 (24)	1.757 (15)		
Diethyl phosphorothioic acid	1.683 (25)	1.691 (26)	1.734 (29)	1.762 (23)		
Diethyl phosphorodithioic acid	1.684 (23)	1.693 (28)	1.730 (25)	1.761 (17)		
Ethanol		1.698 (18)	1.735 br (18)	1.766 (13)		
Diethyl oxalate	1.678 (21)	1.692 (21)	1.722 (19)	1.752 (9)		
Diethyl carbonate	1.668 (22)	1.682 (23)	1.712 (20)	1.749 (12)		
SSS-Triethyl phosphorotrithioate	1.687 (26)	1.695 (26)	1.740 (42)			
Ethyl mercaptan		1.690 (33)	1.739 (65)			
B region						
Triethyl phosphite	2.265 (119)	2.305 (138)	2.344 (64)	2.411 (60)	2.453 (78)	2.482 (77)
Triethyl phosphorothionate	2.261 (199)	2.303 (145)	2.343 (78)	2.410 (47)	2.458 (58)	2.483 (60)
Triethyl phosphate	2.260 (122)	2.304 (91)	2.339 (48)	2.410 (47)	2.458 (58)	2.483 (60)
Diethyl hydrogen phosphonate	2.269 (175)	2.302 (128)	2.348 (72)	2.406 (73)	2.454 (90)	2.487 (72)
Ethyl phosphorodichloridothionate	2.258 (189)	2.298 (107)	2.340 (98)	2.410 (86)	2.449 (93)	2.483 (91)
Diethyl phosphoroamidate	2.261 (171)	2.303 (133)	2.341 (77)	2.411 (79)	2.458 (98)	2.481 (95)
Diethyl hydrogen phosphonothioate	2.261 (169)	2.302 (137)	2.341 (79)	2.412 (75)	2.450 (88)	2.477 (71)
Diethyl phosphorochloridothionate	2.258 (182)	2.302 (132)	2.338 (82)	2.409 (73)	2.451 (89)	2.481 (80)
Diethyl phosphorothioic acid	2.263 (181)	2.302 (157)	2.339 (99)	2.411 (97)	2.452 (111)	2.481 (113)
Diethyl phosphorodithioic acid	2.262 (180)	2.302 (140)	2.342 (83)	2.412 (77)	2.450 (94)	2.483 (83)
Ethanol	2.270 (110)	2.305 (137)	2.362 (72)	2.419 (59)	2.366 (87)	
Diethyl oxalate	2.257 (174)	2.302 (123)	2.346 (67)	2.408 (80)	2.441 (93)	2.483 (56)
Diethyl carbonate	2.250 (162)	2.294 (139)	2.342 (87)	2.431 (77)		2.474 (54)
		2.312 (87)	2.385 (69)			
SSS-Triethyl phosphorotrithioate	2.268 (133)	2.284 (121)	2.304 (172)	2.362 (101)	2.397 (70)	2.432 (26)
			2.453 (42)	2.484 (51)	2.502 (43)	2.512 (50)
Ethyl mercaptan	2.274 (138)	2.285 (132)	2.308 (182)	2.365 (99)	2.396 (66)	2.432 (16)
					2.455 (65)	2.488 (56)

TABLE XIII

n-PrO BANDS

Compound	Band positions in μ ($\epsilon \times 10^2$)								
A region									
Di-*n*-propyl phosphorochloridothionate			1.697 (27)		1.729 (27)		1.755 (20)		
Di-*n*-propyl phosphorodithioic acid			1.699 (26)		1.731 (26)		1.754 (20)		
n-Propyl phosphorodichloridothionate			1.698 (26)		1.729 (28)		1.753 (21)		
B region									
Di-*n*-propyl phosphorochloridothionate	2.268 (164)	2.302 (156)	2.314 (138)	2.348 (104)	2.365 (87)	2.389 (78)	2.431 (96)	2.447 (101)	2.488 (91)
Di-*n*-propyl phosphorodithioic acid	2.273 (166)	2.301 (151)	2.313 (133)	2.349 (103)	2.369 (90)	2.388 (82)	2.425 (88)	2.447 (99)	2.487 (95)
n-Propyl phosphorodichloridothionate	2.266 (141)	2.297 (152)	2.311 (135)	2.347 (103)	2.364 (96)	2.387 (81)	2.422 (93)	2.447 (98)	2.487 (93)

TABLE XIV

A. *i*-PrO BANDS

Compound	Band position in μ ($\epsilon \times 10^2$)								
A region									
Triisopropyl phosphite	1.684 (28)	1.696 (33)	1.733 (24)	1.767 (14)	1.799 (10)				
Diisopropyl phosphorochloridothionate	1.683 (26)	1.692 (36)	1.730 (26)	1.755 br (13)	1.800 (11)				
Diisopropyl phosphorodithioic acid	1.680 (28)	1.692 (36)	1.731 (22)	1.755 (12)	1.802 (10)				
Isopropyl phosphorodichloridothionate	1.679 (29)	1.689 (41)	1.729 (31)	1.752 (17)	1.798 (13)				
Isopropyl alcohol	1.687 (28)	1.699 (25)	1.736 (22)	1.767 (15)	1.824 (12)				
B region									
Triisopropyl phosphite	2.268 (140)	2.300 (163)	2.326 (165)	2.346 (89)	2.409 (108)	2.437 (114)	2.462 (109)	2.420 (104)	
	2.511 sh (45)	2.543 (51)	2.594 (45)						
Diisopropyl phosphorochloridothionate	2.265 (150)	2.294 (173)	2.320 (178)	2.341 (102)	2.402 (125)	2.430 (128)	2.452 (116)	2.477 (84)	
	2.514 (65)	2.550 (45)	2.584 (48)						
Diisopropyl phosphorodithioic acid	2.265 (144)	2.295 (165)	2.321 (166)	2.343 (101)	2.403 (115)	2.433 (119)	2.453 (110)	2.475 (110)	
	2.526 (58)	2.558 (47)	2.587 (42)						
Isopropyl phosphorodichloridothionate	2.264 (160)	2.292 (168)	2.319 (180)	2.341 (104)	2.401 (137)	2.428 (137)	2.452 (130)	2.478 (83)	
	2.519 (74)	2.551 (59)	2.584 (58)						
Isopropyl alcohol	2.269 (137)		2.316 (199)		2.422 (122)		2.472 (143)		

TABLE XIV (*concluded*)

B. *n*-BuO BANDS

Compound	Band positions in μ ($\epsilon \times 10^2$)							
A region								
Dibutyl hydrogen phosphonate	1.693 sh (23)	1.703 (36)	1.715 (32)	1.731 (29)	1.752 (28)			
Tributyl phosphate	1.692 sh (23)	1.702 (34)	1.716 (30)	1.732 (28)	1.752 (27)			
Tributyl phosphite	1.695 sh (22)	1.704 (32)	1.713 (33)	1.737 (26)	1.747 (28)			
Dibutyl phosphorodithioic acid	1.693 sh (25)	1.703 (35)	1.712 (31)	1.733 (30)	1.751 (28)			
Butyl phosphorodichloridothionate	1.690 sh (24)	1.703 (33)	1.712 (30) 1.718 (30)	1.730 (31)	1.747 (29)			
Dibutyl phosphorochloridothionate	1.694 sh (24)	1.702 (33)	1.713 (28) 1.721 (28)	1.731 (29)	1.750 (27)			
B region								
Dibutyl hydrogen phosphonate	2.268 (145)	2.305 (72)	2.348 (121)	2.384 (112)	2.437 (115)	2.452 (127)	2.483 (99)	2.505 (81)
Tributyl phosphate	2.268 (152)	2.304 (172)	2.347 (123)	2.386 (112)	2.437 (114)	2.450 (112)	2.488 (103)	2.504 (99)
Tributyl phosphite	2.270 (151)	2.307 (171)	2.350 (115)	2.388 (112)	2.437 (107)	2.454 (121)	2.488 (93)	2.505 (86)
Dibutyl phosphorochloridothionate	2.270 (165)	2.303 (178)	2.347 (133)	2.386 (119)	2.433 (120)	2.452 (134)	2.487 (107)	2.504 (98)
Dibutyl phosphorodithioic acid	2.271 (174)	2.305 (190) 2.285 (138)	2.348 (144)	2.384 (131)	2.437 (127)	2.451 (137)	2.482 (111)	2.503 (100)
Butyl phosphorodichloridothionate	2.266 (170)	2.301 (182)	2.348 (132)	2.385 (109)	2.437 (109)	2.450 (132)	2.485 (100)	2.503 (101)

TABLE XV

i-Pr_2N COMPOUNDS, μ ($\epsilon \times 10^2$)

i-$Pr_2NP(S)(OEt)_2$	*i*-$Pr_2NP(S)(O\,n\text{-}Pr)_2$	*i*-$Pr_2NP(S)(O\,i\text{-}Pr)_2$	*i*-$Pr_2NP(S)(O\,n\text{-}Bu)_2$
A region			
1.687 (98)	1.689 (90)	1.688 (82)	1.690 (85)
1.698 (110)	1.699 (123)	1.697 (120)	1.699 (104)
1.735 (104)	1.721 (26)	1.734 (100)	1.721 (88)
1.764 (58)	1.736 (101)	1.764 (61)	1.737 (95)
1.807 (29)	1.758 (76)	1.806 (38)	1.759 (85) br
	1.808 (37)		1.808 (38)
B region			
2.267 (519)	2.276 (535)	2.268 (498)	2.274 (482)
2.303 (646)	2.303 (674)	2.302 (706)	2.304 (644)
2.342 (276)	2.346 (340)	2.313 (600) wk, sh	2.340 (364)
2.360 (280)	2.388 (364)	2.341 (348)	2.399 (361)
2.406 (302) br	2.401 (332)	2.362 (276)	2.405 (368)
2.447 (290) br	2.447 (340)	2.404 (425)	2.443 (240)
2.467 (286)	2.462 (328)	2.434 (372)	2.466 (407)
2.482 (234)	2.587 (160) wk	2.462 (368)	2.505 (433)
2.502 (212)		2.587 (179)	2.545 (182)
2.548 (157)			
2.586 (124) wk			

SEPARATIONS OF THE PLATINUM METALS BY ION EXCHANGE[1]

S. S. Berman and W. A. E. McBryde

ABSTRACT

Distribution coefficients for the chlorides of ruthenium, rhodium, palladium, iridium(III and IV), and platinum have been determined between the anion exchanger Amberlite IRA-400 and hydrochloric acid solutions of various molarities. Separations of various combinations of rhodium, iridium, palladium, and platinum in amounts of 0.5 mg. or less are described. When, in the course of these separations, the four metals are present together, special procedures are required to ensure complete recovery of platinum.

There have been several attempts to employ ion exchange in the separation of the platinum metals, but only a limited degree of success has been achieved. MacNevin and Crummett (1) suggested that a separation of rhodium, iridium, palladium, and platinum might be possible owing to the graded stabilities of the chloride and ammine complexes of these metals, but presented no experimental data. Another report by the same authors (2) elaborated on a separation of iridium from palladium achieved by converting the palladium to a cationic diammine, leaving the iridium as an anion, and separating the two on this basis. Stevenson *et al.* (3) submitted a note on the separation of the four metals on the cation exchanger Dowex-50, based on the formation of perchlorates of these metals by fuming their solutions with perchloric acid. No data were given, but this separation is of questionable value because of the inability to keep even milligram quantities of platinum and iridium from precipitating in this medium. Blasius and Wachtel (4) achieved separations of platinum from the other three metals by adsorbing the platinum complex on the anion exchanger Permutit-ES in the hydroxide form. The other three metals were eluted by a solution of sodium hydroxide, and the platinum recovered by elution with nitric acid. MacNevin and McKay (5) have prepared spectrographically pure rhodium through the formation of a cationic rhodium species, the other metals being left as anions. This separation is not quantitative. The separations of rhodium and iridium have been discussed in a previous paper (6).

The only equilibrium data recorded concerning the behavior of platinum metal complexes toward ion exchangers are those of Kraus *et al.* (7). These workers measured the distribution coefficients of chloroplatinate (IV) and chloropalladate (II) relative to the anion exchanger Dowex-1 in hydrochloric acid solutions.

In the following report the measurement of the distribution coefficients of ruthenium, rhodium, iridium, palladium, and platinum in hydrochloric acid solutions relative to the anion exchanger Amberlite IRA-400 is described, as well as a series of separations of these metals.

EXPERIMENTAL

Standard Solutions

Palladium.—A stock solution was prepared by dissolving pure palladium sponge in aqua regia, evaporating several times to dryness with hydrochloric acid, and then dissolving the residue and diluting with 0.1 *M* hydrochloric acid. This solution was standardized gravimetrically by precipitation with salicylaldoxime (8). Analyses for palladium were generally made colorimetrically by the potassium iodide method (9),

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Contribution from the Department of Chemistry, University of Toronto, Toronto 5, Ontario, Canada.

but very small amounts (less than 10 μg.) were determined by the *p*-nitrosodimethylaniline procedure (10).

Platinum.—The stock solution was prepared by the dissolution of pure platinum sponge in aqua regia and treatment similar to that described for palladium. The solution was standardized by precipitation with 4-phenylthiosemicarbazide (11). Colorimetric analyses were made by the tin(II) chloride method (12).

Ruthenium.—A stock solution was prepared in 0.5 *M* hydrochloric acid from ammonium chlororuthenate crystallized from a solution of sodium chlororuthenate in hydrochloric acid. The solution was standardized by the evaporation of a measured quantity, followed by reduction of the salt to metallic ruthenium with hydrogen. Analyses were made colorimetrically by the thiourea procedure (13).

Rhodium and Iridium.—The preparation of standard solutions of these metals is described in a previous paper (6).

The Resin and Columns

The resin used in this research was Amberlite IRA-400 in an analytical grade. The dried resin was ground to yield fractions of various degrees of fineness. The portion of mesh size 70 to 100 was used for the measurement of distribution coefficients. It was found to be hygroscopic, and was dried at 100° C. prior to weighing, and was stored over anhydrous magnesium perchlorate. The exchange capacity was found to be 3.78 meq. per gram of dry resin. This was determined for 5.00-g. samples by the procedure of Fisher and Kunin (14).

For column work the resin of <100 mesh was used. The manner of preparing the resin to rid it of fine particles has been described in a previous paper (6). The columns were of conventional design in two sizes, having internal diameters of 10 mm. and 5 mm. respectively. The depth of resin in the bed varied among the different experiments, and is stated in the description of each. The flow of liquid through the beds was maintained at about 50 ml. per hour.

Measurement of Distribution Coefficients

The distribution coefficients of chloropalladate(II), chloroplatinate(IV), chloroiridate (IV), chloroiridate(III), chlororhodate, and chlororuthenate were measured in hydrochloric acid solutions. This was done by shaking a weighed amount, approximately 0.3 g., of resin with measured quantities of platinum metal solutions in 25.0 ml. of hydrochloric acid of various molarities for 40 hours. The mixtures were filtered, and 20.0-ml. aliquots of the filtrates analyzed. The amounts of metal adsorbed on the exchanger were thus found, and the distribution coefficients (amount of metal per kilogram of resin/amount per liter of solution) were calculated. In regions of very high adsorption 300 ml. of acid solution was used, and 250-ml. aliquots taken for analysis.

TABLE I

DISTRIBUTION COEFFICIENTS

	D					
HCl, *M*	Rh	Ru	Ir(III)	Ir(IV)	Pd(II)	Pt(IV)
0.1	15	180	1050	186000	45000	44000
0.5	12	88	350	59000	15000	27000
1.0	10	40	60	32000	4300	20000
4.0	0	12	2	6000	300	2100
8.0	0	4	0	3200	75	780
12.0	0	0	0	960	35	400

The amounts of resin and solution were selected to limit loading of the resin to no more than 2% of capacity.

The results are summarized in Table I and in Fig. 1.

A comparison of these values with those obtained by Kraus *et al.* (7) for Pd(II) and Pt(IV) shows good agreement in the low-adsorption range where these workers had low degrees of loading. In the high-adsorption range where these workers allowed the loading to become large there is a marked divergence, their distribution coefficients being much lower than those given here.

It is readily seen that Pt(IV) and Ir(IV) are very strongly adsorbed throughout the whole hydrochloric acid range, and Pd(II) at low hydrochloric acid concentrations.

According to Walton (15) practically all ion-exchange distribution data can be expressed by the Rothmund–Kornfeld equation

$$M_x/M_y = K\,((x)/(y))^p,$$

where M_x and M_y are the moles of x and y per gram of exchanger and (x) and (y) are their molar concentrations in solution; K and p are constants. Then by plotting $\log(M_x/M_y)$ against $\log((x)/(y))$ one should obtain a straight line.

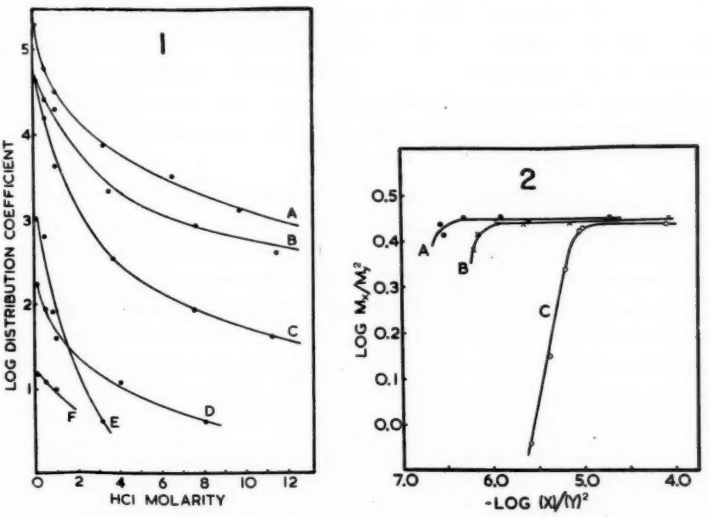

FIG. 1. The distribution coefficients of rhodium, iridium, platinum, palladium, and ruthenium in hydrochloric acid solutions. A: chloroiridate(IV), B: chloroplatinate(IV), C: chloropalladate(II), D: chlororuthenate(III), E: chloroiridate(III), F: chlororhodate.

FIG. 2. The distribution data plotted according to the Rothmund–Kornfeld equation. A: chloroiridate (IV), B: chloroplatinate(IV), C: chloropalladate(II).

This is, more or less, what happened when the data for Rh, Ru, and Ir(III) were plotted. However, the three other complexes produced interesting curves (Fig. 2). In regions of very high adsorption M_x/M_y^2 (the squared term arises since these complexes are doubly charged) is seen to be almost independent of the concentration ratio of complex to chloride in solution; i.e., $p \approx 0$.

This might indicate that in these instances simple exchange equilibria are not taking place and that some mechanism other than ion exchange is the predominant factor.

An analogy may be seen here between this strong adsorption and the solubility of quaternary amine platinum metal chlorides. It is well known that Pt(IV) and Ir(IV) form relatively insoluble salts with quaternary amines of the type $(R_4N)_2PtCl_6$. Since the anion exchanger is in effect a polystyrenedivinylbenzene quaternary amine, it may be that the same forces that produce the insoluble salts contribute to the strong adsorption of these complexes on the resin. Palladium(II) is known to form a number of insoluble diammine dichloride complexes, the solubility of which is greater in concentrated hydrochloric acid than in neutral solution. The behavior of palladium toward the resins may be, in the same fashion, compared with the formation of ammine precipitates of this sort.

To further illustrate this analogy 5 ml. of 0.2 *M* tetrabutylammonium chloride was added to 10 mg. of each of the six complexes in 5 ml. of 0.5 *M* hydrochloric acid. Precipitates formed in the tubes containing Pd(II), Pt(IV), and Ir(IV). When 1 ml. of concentrated hydrochloric acid was added to each of these, the palladium precipitate dissolved instantly and the iridium precipitate partially dissolved. Further addition of hydrochloric acid resulted in the complete dissolution of the iridium precipitate, but the platinum precipitate could only be partially dissolved by this means.

While the above experiment does not prove that stable resin–platinum metal compounds are formed analogous to insoluble precipitates, the parallel between these observations and subsequent column experiments was striking. For example, it was possible to remove Pd(II) from the resin by elution with concentrated hydrochloric acid. Pt(IV) and Ir(IV) cannot be completely recovered by this means. The iridium complex may be removed by a hot extraction with hydrochloric acid, but even this rather violent treatment will only partially remove the platinum complex.

The Separation of Palladium and Platinum

The purpose of this research was to develop an ion-exchange procedure for this separation which could be integrated with the rhodium–iridium separation previously reported (6). Also, the recovery of Pd(II) and Pt(IV) from anion exchangers by a wet method has long been a problem and an obstacle in the application of anion exchange in the separation of platinum from base metals.

It was confirmed that Pd(II) and Pt(IV) can be quantitatively adsorbed from dilute hydrochloric acid solutions on an anion exchanger, Amberlite IRA-400.

The Recovery of Palladium

Five milliliters of 1 *M* hydrochloric acid containing approximately 500 γ of palladium were fed onto 2.5-cm. resin beds in the larger columns which had been previously washed with 25 ml. of the acid solution. Complete recovery of the palladium was achieved by 100 ml. of 12 *M* hydrochloric acid.

Number of experiments	5
Palladium taken	478 γ
Palladium recovered (range)	476–480 γ (see Fig. 3)

It was found that no platinum was eluted provided these beds were at least 2.3 cm. deep.

The work was repeated with 3-cm. beds in the smaller columns. Complete recovery was achieved by 40 ml. of 12 *M* hydrochloric acid or by 60 ml. of 9 *M* acid (see Fig. 3). The use of 6 *M* acid resulted in too much tailing to be of value. However, it was found that 40 ml. of 12 *M* hydrochloric acid eluted much platinum, whereas 60 ml. of 9 *M* acid eluted none.

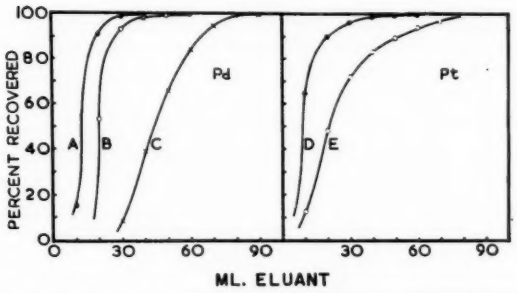

FIG. 3. Some typical elution curves for chloropalladate(II) and chloroplatinate(IV). A: chloropalladate(II) eluted with 12 *M* hydrochloric acid solution (small column), B: chloropalladate(II) eluted with 9 *M* hydrochloric acid solution (small column), C: chloropalladate(II) eluted with 12 *M* hydrochloric acid solution (large column), D: chloroplatinate(IV) eluted with 2.4 *M* perchloric acid solution (small column), E: chloroplatinate(IV) eluted with 15% (w/v) zinc chloride in 9 *M* hydrochloric acid solution at 96° C. (large column).

It was also shown that Pd(II) could be easily recovered by elution with dilute perchloric acid solutions. The recoveries observed for elution with 40 ml. of 0.5 *M* perchloric acid were as follows:

Number of experiments	3
Palladium taken	478 γ
Palladium recovered	478–481 γ

Since perchloric acid was later shown to be a good eluant for Pt(IV) this reagent cannot be used to separate the two metals.

Recovery of Platinum

Platinum was fed onto 2.5-cm. resin beds in the larger columns in a manner similar to the palladium.

It was verified that solutions of hydrochloric, nitric, or sulphuric acids, either dilute or concentrated, elute only part of the Pt(IV). The same is true for ammoniacal eluants. Working at elevated temperatures produced only minor improvements in the recoveries.

Kraus and his co-workers (7, 16) noted the high affinities of zinc and cadmium chloride in hydrochloric acid solutions toward anion exchangers. Preliminary experiments with 2.5 *M* solutions of both these salts in 9 *M* hydrochloric acid showed better recoveries of platinum than had been previously achieved. It was found that 93% of the Pt(IV) could be recovered by the zinc chloride solution, and that quantitative recoveries could be achieved if the column were surrounded with a hot-water jacket at 96° C. The following recoveries were made by elution with 90 ml. of a 15% (w/v) solution of zinc chloride in 9 *M* hydrochloric acid at 96° C. (see also Fig. 3).

Number of experiments	3
Platinum taken	490 γ
Platinum recovered	488–494 γ

Experiments showed that the Pt(IV) could also be quantitatively recovered by 90 ml. of 2.4 *M* perchloric acid. The same observation was made with 3-cm. resin beds in the smaller columns; in these cases the platinum was recovered by 60 ml. of the 2.4 *M* perchloric acid (see Fig. 3).

Number of experiments	7
Platinum taken	490 γ
Platinum recovered (4 cases)	488–492 γ (l)*
(3 cases)	488–490 γ (s)*

*l means larger column, s smaller.

Attempts to recover the Pt(IV) by a Soxhlet extraction were unsuccessful. Extraction with 6 *M* hydrochloric acid produced recoveries of only about 30%. Recoveries of about 90% were achieved with 8 *M* nitric acid.

The recovery of platinum by ashing the exchanger was also investigated. This method had previously been reported as successful by Sussman *et al.* (17) but no data were given. The resin containing the adsorbed Pt(IV) and the glass wool plug were transferred to a small crucible and dried under a heat lamp. The crucible was placed in a furnace at 300° C. and the temperature raised to 900° over the course of an hour. The crucible was removed, cooled, and set over a boiling-water bath for 1 hour after the addition of 3 or 4 ml. of aqua regia. There was no residue evident in the crucible after this treatment save for the bit of fused glass wool. Results of the analysis of this solution after filtration are given below, and indicate that this procedure is a simple and satisfactory one for the recovery of the metal.

Number of experiments	3
Platinum taken	490 γ
Platinum recovered	491–492 γ

Separation of Palladium and Platinum

Separations were carried out in both large and small columns. Mixtures of the metals containing 6 mg. of sodium chloride (to prevent baking of the metal on the bottom of the beaker) were evaporated to dryness and the residue dissolved in one or two milliliters of water. This solution was fed onto the resin bed with a dropper. The larger beds were 2.5 cm. deep and were eluted with 100 ml. of 12 *M* hydrochloric acid followed by 90 ml. of 2.4 *M* perchloric acid. The smaller columns contained resin beds 3 cm. deep, and were eluted with 60 ml. of 9 *M* hydrochloric acid followed by 75 ml. of 2.4 *M* perchloric acid. The results are summarized below:

Number of experiments	7	2
Platinum taken	490 γ	98 γ
Platinum recovered (4 cases)	487–496 γ (l)	
(3 cases)	490–491 γ (s)	97–102 γ
Palladium taken	478 γ	96 γ
Palladium recovered (4 cases)	468–480 γ (l)	
(3 cases)	476–478 γ (s)	95–96 γ

Separations of Various Mixtures of Platinum Metals in Solution

From the satisfactory results obtained in the rhodium–iridium and palladium–platinum separations it was felt that separations of all combinations of the four metals could be achieved, although separations of mixtures containing both rhodium and iridium would obviously have to be carried out in two stages. This turned out to be an overly optimistic assumption when iridium, palladium, and platinum are all present, but, generally, some very satisfactory separations were made.

Rhodium and Palladium

This separation was first done on 2.3-cm. beds in the larger columns. The beds were washed prior to use with 10 ml. of 2 *M* hydrochloric acid. A solution containing the two metals in 5 ml. of 2 *M* hydrochloric acid was fed onto the bed, and the latter eluted with 90 ml. of the acid solution to remove the rhodium. Elution was continued with 100 ml. of 12 *M* hydrochloric acid to recover the palladium. A previous experiment showed that no palladium was eluted by 90 ml. of the 2 *M* hydrochloric acid. The results of this separation are tabulated below.

Further separations were carried out in the smaller columns with 3-cm. resin beds which were previously washed with 10 ml. of 2 *M* hydrochloric acid. In this case the solutions

were evaporated to dryness with 6 mg. of sodium chloride, redissolved in one or two milliliters of water, and fed onto the bed with a dropper. Elutions were made with 50 ml. of 2 *M* hydrochloric acid followed by 50 ml. of 9 *M* hydrochloric acid. The results are included in the following table.

Number of experiments	6
Rhodium taken	499 γ
Rhodium recovered (3 cases)	499–500 γ (l)
(3 cases)	500–501 γ (s)
Palladium taken	478 γ
Palladium recovered (3 cases)	478–479 γ (l)
(3 cases)	476–478 γ (s)

It was noticed in this separation that as the rhodium was being eluted with the 2 *M* hydrochloric acid the palladium band slowly moved and diffused part way down the bed. This is the only instance in this work where a platinum metal band was seen to move. Owing to this partial migration it was possible to recover the palladium with 40 ml. of 9 *M* hydrochloric acid (Fig. 4) in contrast to the 60 ml. needed in the palladium–platinum separation.

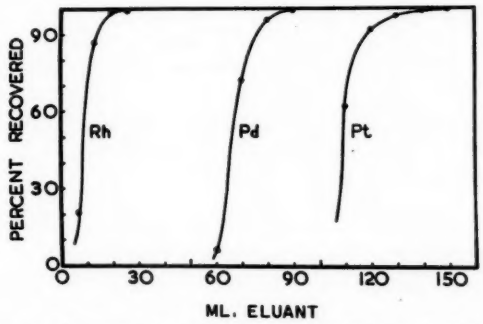

FIG. 4. Elution curves for the separation of rhodium, palladium, and platinum (small column). Rh: eluted with 50 ml. 2 *M* hydrochloric acid solution, Pd: eluted with 50 ml. 9 *M* hydrochloric acid solution, Pt: eluted with 75 ml. of 2.4 *M* perchloric acid solution.

Rhodium and Platinum

This separation was not attempted, but since the separation of rhodium, palladium, and platinum is feasible (see below) there is no reason why it should not be easily accomplished.

Iridium and Palladium

This separation was done in the larger columns in a manner similar to the separation of rhodium and palladium. The iridium was reduced to the tervalent state by hydroxylamine prior to feeding onto the column. The bed was eluted with 90 ml. of 2 *M* hydrochloric acid to recover the iridium, and then 100 ml. of 12 *M* hydrochloric acid for the palladium. The results are summarized as follows:

Number of experiments	3
Iridium taken	454 γ
Iridium recovered	452–454 γ
Palladium taken	478 γ
Palladium recovered	474–478 γ

Iridium and Platinum

This separation was not tried, but experiments described below indicate that it is quite feasible.

Rhodium, Palladium, and Platinum

One separation of these three metals was made to gather data for Fig. 4. This is the only three-metal separation that can be made with only one column. A solution containing the three metals was evaporated to dryness with 6 mg. of sodium chloride. The residue was redissolved in 2 ml. of 2 *M* hydrochloric acid solution and fed with a dropper onto a small 3-cm. resin bed which had been previously washed with 10 ml. of the acid solution. The bed was eluted with 50 ml. of 2 *M* hydrochloric acid, followed by 50 ml. of 9 *M* hydrochloric acid, and then 70 ml. of 2.4 *M* perchloric acid.

Rhodium, Iridium, and Palladium

Solutions of these three metals were evaporated to dryness with 6 mg. of sodium chloride and the residues redissolved in 1 ml. of water. The iridium was reduced with a few drops of 1% hydroxylammonium chloride solution, and the solutions fed onto 3-cm. beds in small columns. These beds had been previously washed with 10 ml. of 2 *M* hydrochloric acid. The beds were eluted with 80 ml. of the acid solution to recover the rhodium and iridium, followed by 50 ml. of 9 *M* hydrochloric acid for the palladium. The first effluents were evaporated to dryness and the residues redissolved in 2 ml. of 0.8 *M* hydrochloric acid (also containing cerium(IV) sulphate at a concentration of 0.001 *M*). These solutions were fed with a dropper onto small columns containing 3-cm. beds of resin which had been prepared with quadrivalent cerium, and the rhodium–iridium separation was carried out as described in the previous communication (6).

The procedure was repeated but the palladium was eluted with 50 ml. of 0.5 *M* perchloric acid. The rhodium and iridium were not determined in these experiments. The various results are summarized below.

Number of experiments	3
Iridium taken	454 γ
Iridium recovered	451–456 γ
Rhodium taken	499 γ
Rhodium recovered	495–500 γ
Palladium taken	478 γ
Palladium recovered	476–479 γ (eluted with HCl) 476–479 γ (3 eluted with $HClO_4$)

Rhodium, Iridium, and Platinum

The procedure was exactly as described above except that the beds were eluted with 80 ml. of 2 *M* hydrochloric acid followed by 75 ml. of 2.4 *M* perchloric acid for the platinum.

Number of experiments	3
Iridium taken	454 γ
Iridium recovered	451–456 γ
Rhodium taken	499 γ
Rhodium recovered	498–501 γ
Platinum taken	490 γ
Platinum recovered	490–492 γ

Rhodium, Iridium, Palladium, and Platinum

Solutions containing these four metals were evaporated to dryness with 6 mg. of sodium chloride, and the residues redissolved in 1 ml. of water. A few drops of hydroxylamine solution were added to reduce the iridium, and the solutions were then fed onto 3-cm. beds in small columns. The beds were eluted with 80 ml. of 2 *M* hydrochloric acid followed by 50 ml. of 9 *M* hydrochloric acid, and then with 75 ml. of 2.4 *M* perchloric acid. The first effluents were treated for a separation of rhodium and iridium as described above. Good results were obtained for the recovery of rhodium, iridium, and palladium, but the platinum recoveries were all low by about 25%.

Further examination showed that some platinum was being eluted along with the palladium but had not been noticed since this small quantity produced a negligible interference in the palladium determinations. It is believed that this early elution of the platinum was due to a partial reduction of the quadrivalent metal to the bivalent state by the hydroxylamine used to reduce the iridium. The bivalent platinum evidently has much the same affinity for the resin as the bivalent palladium.

An unsuccessful search was made for a reducing agent which would reduce the quadrivalent iridium but not any of the quadrivalent platinum. Best results (94% recovery of the platinum in the "platinum fraction") were obtained by the slow reduction of the iridium in neutral solution by sodium oxalate.

An attempt to reoxidize the platinum on the exchanger with cerium(IV) after the removal of the tervalent iridium was also unsuccessful.

One separation of the four metals was carried out in which the "palladium fraction" was evaporated to a few milliliters, boiled with nitric acid to oxidize the platinum, and evaporated twice to dryness with hydrochloric acid. The residue was dissolved in a few milliliters of 2 *M* hydrochloric acid, and this solution treated as described above for the separation of palladium and platinum. In this way platinum was completely recovered in two fractions.

	Taken	Found
Rhodium	499 γ	501 γ
Iridium	454 γ	451 γ
Palladium	478 γ	479 γ
Platinum	490 γ	363 plus 127 = 490 γ

Hydrolytic Separation of Rhodium, Iridium, and Palladium from Platinum on a Microgram Scale

The generally accepted procedure of precipitating rhodium, iridium, and palladium as hydrated oxides as a method of separating these metals from platinum has never been applied on a microgram scale. In view of the relative difficulty encountered in the four-metal separation described above it was decided to investigate the possibility of removing the platinum by this method prior to applying an ion-exchange separation for the remaining three metals.

The procedure followed was generally that described in *Applied inorganic analysis* (18), pp. 376–377, except that a carrier was employed to aid in the precipitation of the small quantities of the metals present. Both titanium(IV) sulphate and cerium(IV) sulphate were used for this purpose. The cerium salt was finally chosen because its precipitate was easier to handle.

A solution of platinum was evaporated to dryness with 6 mg. of sodium chloride in a 30-ml. beaker. The residue was dissolved in 1 ml. of 2 *M* hydrochloric acid and diluted to about 5 ml. with water. The solution was then heated to boiling and about 5 mg. of cerium(IV) sulphate was added followed by 5 ml. of a filtered solution of sodium bromate. A filtered 10% solution of sodium bicarbonate was added slowly until the first trace of a permanent precipitate formed. Then 5 ml. more of the sodium bromate solution was added. Addition of bicarbonate was continued until no further precipitation was evident. Another 5 ml. of bromate solution was added, and the mixture was boiled for 10 minutes. The mixture was allowed to cool, the precipitate to settle, and the whole was then filtered through a porcelain filter crucible of medium porosity. The precipitate was washed with 0.1 *M* sodium chloride solution. The filtrate was boiled with hydrochloric acid to destroy the bromate, and analyzed for platinum. Complete recovery of the platinum was obtained.

Solutions of the four metals were treated as above, and again all the platinum was found in the filtrates, indicating its separation from the other three metals.

The oxide precipitate from one of these experiments was dissolved in concentrated hydrochloric acid, evaporated to dryness, and the three metals separated as described above. A quantitative separation of the four metals was accomplished by this means.

	Taken	Found
Rhodium	499 γ	502 γ
Iridium	454 γ	451 γ
Palladium	478 γ	481 γ
Platinum	490 γ	492 γ

These experiments indicate that the ion-exchange separations may be integrated with a Gilchrist–Wichers type of scheme (18) for the analysis of the platinum metals on a microgram scale.

Separation of Rhodium and Ruthenium

It has been noted that this separation is of interest to radiochemists since rhodium is a daughter of ruthenium by beta decay. Some qualitative experiments were made to determine the feasibility of making the separation by ion exchange.

Ruthenium behaves toward the exchanger much like iridium. The quadrivalent complex is strongly adsorbed but appears to be partially reduced by the resin so that relatively large losses occur in the feed effluent. This can be remedied by the addition of an oxidant such as cerium(IV) to the feed solution. Attempts to elute the quadrivalent ruthenium with hydrochloric acid were unsuccessful, as was an attempt to reduce it on the resin with a 1% solution of hydroxylammonium chloride. The tervalent complex has a very low affinity for the resin, and a separation of it from tervalent rhodium does not seem to be possible.

It is possible that a procedure similar to that evolved for the separation of rhodium and iridium could be developed to separate the two metals in solution, but the problem of the quantitative removal of the quadrivalent ruthenium from the resin requires further study.

ACKNOWLEDGMENTS

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THE SEPARATION OF RHODIUM AND IRIDIUM BY ION EXCHANGE[1]

S. S. Berman and W. A. E. McBryde

ABSTRACT

Separations of rhodium and iridium as chlorides by means of columns of the anion exchanger Amberlite IRA-400 are described. Iridium is maintained in the quadripositive state by the addition of cerium(IV), the presence of which is necessary to counteract the reducing action of the resin. The marked difference in affinity toward the resin of Ir(IV) and Rh(III) makes the separation possible. Rhodium can easily be eluted from the resin by 2 *M* hydrochloric acid. Removal of all the iridium from the resin is accomplished in a Soxhlet extractor with 6 *M* hydrochloric acid. A number of less successful procedures for this separation are discussed.

In recent years there have appeared several procedures employing ion-exchange resins for the separation of rhodium and iridium, an operation which may be regarded as the most difficult step in the analysis of the elements of the platinum metal group. Cluett *et al.* (1) proposed a method applicable to mixtures containing 10 mg. or more of each of the metals. This method can be criticized on two accounts. Removal of iridium from the exchanger required the use of large quantities of salts and acids which must be destroyed prior to the determination of the iridium. Also, losses of iridium in the feed solution indicated that attempts to use the procedure for smaller quantities of the metals would lead to relatively appreciable quantities of iridium remaining with the rhodium. The method of Berg and Senn (2) which separates the metals on the basis of oppositely-charged thiourea complexes suffers from the time-consuming necessity of destroying the thiourea prior to the analysis of the rhodium and iridium. MacNevin and McKay (3) claim to produce spectrographically pure rhodium from a rhodium–iridium mixture, but the separation is not quantitative.

The purpose of this work was to develop a relatively simple quantitative separation of the two metals which would lend itself to their subsequent analysis without difficulty. This separation is necessary, since, to date, no satisfactory specific reagent for either of these elements has been found.

The procedure described below is based, like that of Cluett *et al.*, on the strong affinity of chloroiridate(IV) toward the anion exchanger in contrast with the relatively weak affinity of the chlororhodate complex. Losses of iridium in the feed solution have been eliminated by the choice of a suitable oxidant, and a simple method of extraction of the iridium complex from the resin has been developed.

EXPERIMENTAL

Apparatus and Solutions

Stock solutions of rhodium and iridium were prepared by dissolving highly refined chloro salts, which had been obtained from the International Nickel Company of Canada, respectively in 0.05 *M* and 0.1 *M* hydrochloric acid. The rhodium solution was standardized gravimetrically (4) and the iridium solution volumetrically (5). These solutions contained approximately two milligrams of metal per milliliter of solution. They were diluted 20-fold with 0.1 *M* hydrochloric acid in the following work.

Two sizes of columns, of conventional design, were used. The larger were 10 mm. in internal diameter and about 20 cm. in height; the smaller were 5 mm. in internal diameter and about 12 cm. in height. A flow rate of about 50 ml. per hour was used.

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Contribution from the Department of Chemistry, University of Toronto, Toronto 5, Ontario, Canada.

The resin used was Amberlite IRA-400 of an analytical grade. Conversion to the chloride form was ensured by stirring the resin for several hours with a large excess of 2 *M* hydrochloric acid. At the same time the resin was freed of small bits of foreign matter which usually floated on the surface of the supernatant liquid. The resin was dried at 110° C. and ground to yield two fractions, one of which was of mesh size 70 to 100 and the second of mesh size less than 100. The latter fraction was freed of very fine particles by shaking with the acid solution, allowing the bulk of the resin to settle, and pouring off the fines. This was repeated until the resin settled completely within a few minutes. The resin was stored in a solution of 2 *M* hydrochloric acid.

In some experiments the iridium was removed from the resin by a Soxhlet extraction. For this purpose a microextractor was used, Corning No. 3860.

Methods of Analysis

Determinations of rhodium were made with the colorimetric procedure employing tin(II) chloride described by Sandell (6). Dilutions were made with 2 *M* hydrochloric acid. Optical densities were measured with a Beckman Model DU spectrophotometer at 470 mμ.

Iridium was determined by the tin(II) chloride–hydrobromic acid procedure of Berman and McBryde (7).

The Adsorption of Iridium on the Exchanger

The development of a sensitive colorimetric procedure for the determination of iridium enabled the authors to carry out a more extensive study of the adsorption of quadrivalent iridium on the resin than was previously possible.

It had been previously demonstrated by Cluett *et al.* (1) that maximum adsorption of chloroiridate(IV) by the exchanger necessitated the presence of an oxidizing agent. That the resin is indeed a mild reducing agent was demonstrated by the following experiments.

A solution containing approximately 500 γ of iridium in 5 ml. of 1 *M* hydrochloric acid was fed onto a 3-cm. bed of 70–100-mesh resin, which had been previously washed with a solution of 1 *M* hydrochloric acid. A dark brown band, characteristic of chloroiridate(IV), formed at the top of the bed. After 16 hours of standing the color of the band had appreciably lightened. After 40 hours the band was no longer visible. This seemed to indicate that the quadrivalent iridium had been slowly reduced to the almost colorless tervalent complex. Elution of the resin bed with 100 ml. of 6 *M* hydrochloric acid yielded about 350 γ of iridium in the effluent, indicating that the reduction was not complete.

Ten milliliters of a 0.1 *N* solution of potassium dichromate was fed onto a resin bed, resulting in an orange-red adsorption band at the top of the bed. After a day a green solution, presumably containing tervalent chromium, was seen diffusing down through the bed.

A solution of 0.8 *M* hydrochloric acid containing about 5 mg. of cerium as cerium (IV) sulphate was passed very slowly through a resin bed. The effluent was colorless, characteristic of a solution of cerium(III).

Bromine as the Oxidant

Choice of a suitable oxidant to counteract the effect of the resin is limited by the fact that chloroiridate(IV) is itself a strong oxidant (E^0 = 1.02 v. (8)). The first choice for this purpose was bromine (E^0 = 1.09 v.). Resin beds 2.5 cm. deep were prepared by transferring the 70–100-mesh resin to the larger columns, and shaking with one or two columnfuls of 0.1 *M* hydrochloric acid containing 10% saturated bromine water by

volume. (The resin had been previously extracted with 6 *M* hydrochloric acid in a Soxhlet extractor to minimize color throwing.) Then 454 γ of iridium in 5 ml. of 0.1 *M* hydrochloric acid was fed onto the column. In most of the experiments the bed was washed with a quantity of the bromine water – hydrochloric acid solution prior to the feeding of the iridium solution. After feeding, the resin bed was washed with 20 ml. of this same solution, and was then eluted with more of the solution to simulate the removal of rhodium. The feed and wash effluents and the simulated "rhodium fraction" were collected separately and evaporated to about one milliliter in volume. A few milliliters of 30% hydrogen peroxide solution was added to each to destroy a yellow-colored material in solution which was usually present and presumably came from the resin. The solutions were boiled to expel bromine and excess hydrogen peroxide, evaporated to near dryness, and analyzed for iridium. To check whether the colored species in the iridium analysis was due to iridium and not to some interfering foreign matter, the spectral curve of each sample was examined in the vicinity of 402 mμ and compared with a known iridium spectrum.

In the following account the bromine water – hydrochloric acid solution will be referred to as the feed solution. It is evident from Table I that the losses of iridium may be considerably reduced by substantial pretreatment of the resin bed. Losses in the last three experiments amount to less than 0.25% of the iridium fed onto the bed.

TABLE I

EFFECT OF PRETREATMENT OF RESIN ON ADSORPTION OF 454 γ OF CHLOROIRIDATE(IV)

Columns of feed soln. shaken with resin	Volume of preliminary wash, ml.	Volume of eluant, ml.	Ir in feed and rinse, μg.	Ir in "Rh fraction", μg.
1	0	100	22	4
1	5	100	2.7	7.6
1	80	100	1.5	3.0
2	100	100	1.0	1.8
2	200	70	Combined — 0.0	
2	200	75	Combined — 1.1	
2	200	75	Combined — 1.1	

However, further work showed that 75 ml. of the feed solution would elute only about 90% of a 499-γ rhodium sample treated in a manner similar to the last three experiments described in Table I, and that any procedure which would quantitatively recover the rhodium resulted in a loss of 4 to 5 γ, or approximately 1% of the iridium taken.

It was also shown, by taking a 45.4-γ sample of iridium, that the loss is more or less an absolute one, and not strictly proportional to the quantity of iridium fed. This may be a serious drawback if such a procedure were to be adapted to micro separations, as the relative loss of iridium would be significant.

An explanation of why losses occur in the presence of this oxidant may be based on the following observation. It was noticed that when the bed was washed with a quantity of the feed solution prior to the feeding of the iridium, the bromine was adsorbed from the solution in a red band at the top of the resin bed. When the quadrivalent iridium was fed, the dark brown band due to this complex did not form at the top of the bed but rather directly below the bromine band, indicating that the bromine had occupied sites on the resin and had made them unavailable to the chloroiridate(IV). Since chloroiridate(IV) has an exceptionally high affinity for the resin, the bromine must indeed be very strongly bound, with a resultant decrease in its activity and in its ability to act as

a mobile oxidant toward any iridium that may have been reduced by the resin. The strong affinity of bromine for the resin was further demonstrated by the inability of a sample of resin which had been saturated with bromine to adsorb any chloroiridate(IV).

Substantially the same results were obtained when chlorine was used as the oxidant in place of bromine.

Cerium(IV) as the Oxidant

In view of the above experience with bromine it was decided that a truly effective oxidant would have to be one which would not itself be adsorbed by the exchanger, nor would oxidize chloride at the concentrations of hydrochloric acid used. The only oxidant found which met these conditions was quadrivalent cerium. The use of cerium(IV) limits the acid concentration permissible to the range of 0.5 *M* to 1 *M*. In acid solutions below this range the cerium salts hydrolyze. In solutions more concentrated than this range chloride is oxidized to chlorine.

The oxidizing solution was prepared by adding 1 ml. of 0.1 *M* cerium(IV) sulphate to 100 ml. of 0.8 *M* hydrochloric acid.

Resin beds 2.5 cm. deep were washed with 10 ml. of water and then rinsed with 10 ml. of the cerium solution. The washing with water was found to be essential for the elimination of iridium losses, although the authors can find no plausible explanation for this. Five milliliters of 0.1 *M* hydrochloric acid solution containing 454 γ of iridium was fed onto the beds, which were then eluted with a further 90 ml. of the cerium solution to simulate the removal of rhodium. The feed effluents and the "rhodium fractions" were passed through large cation-exchange beds to remove the cerium, evaporated to near dryness, and analyzed for iridium. A yellow residue was always present which was found to contain iron (presumably from the resin). Examination of the spectra in the vicinity of 402 mμ showed that no iridium was present.

Similar experiments with 499 γ of rhodium showed that this element is quantitatively recovered in the combined feed and eluate solutions. It was also established that cerium interferes but little in the colorimetric determination of rhodium, and need not be removed if a set of appropriate standards is prepared for comparison. If desired, the cerium can easily be removed by passage of the solution through a bed of Dowex-50.

The Recovery of Iridium

The recovery of iridium adsorbed on an anion exchanger has long been a problem. The metal cannot be conveniently recovered by ashing the resin as Sussman *et al.* (9) did for platinum and palladium because of the difficulty in redissolving it for the purpose of analysis. The only successful wet procedure reported is that of Cluett *et al.* (1) which is very time-consuming and extravagant of reagents.

Elution of Iridium by a Reducing Agent

Since the affinity of chloroiridate(III) for the exchanger is small in hydrochloric acid solutions more concentrated than 1 *M* it was thought that it might be possible to reduce the quadrivalent iridium complex on the resin and elute the tervalent species with hydrochloric acid. The choice of reductants is limited by three factors. Iridium is a noble metal; the determination of iridium is impossible in the presence of most metals; and, also, the reductant should not be adsorbed on the exchanger or the same type of situation may result as was experienced with bromine.

Several experiments were conducted using 1% and 4% solutions of hydroxylammonium chloride and hydrazine hydrochloride as the reductants. The iridium solutions were fed in the presence of cerium(IV) as described in the adsorption experiments. The

bed was rinsed with 20 ml. of 0.8 *M* hydrochloric acid to remove the cerium, and then 25 ml. of the reducing solution was passed through, followed by a dilute solution of hydrochloric acid. The two effluents were collected together and several milliliters of 30% hydrogen peroxide solution was added to destroy the reductant. The solutions were evaporated to near dryness to destroy most of the acid, and then were analyzed for iridium.

Results for the two reductants were much the same. Immediately they came in contact with the adsorption band, it disappeared, indicating that reduction had taken place. Recoveries of iridium ranged from 88% to 96%, and did not seem to depend on the concentration of the reducing agent or on the concentration of the hydrochloric acid eluant. It appears that some of the adsorbed iridium is not readily available for reduction. These results compare closely with those obtained with an ammoniacal elution (1) which also involves a reduction process.

Perchloric Acid as an Eluant

It was hoped that the affinity of the perchlorate anion, which is by far the strongest of all common anions for the exchanger (10), would be great enough to displace the chloroiridate(IV) complex.

The resin beds were fed with iridium as described above and then eluted with 100 ml. of a 10% (v/v) solution of perchloric acid. The bands slowly faded and the effluents were the color of chloroiridate(IV). However, recoveries of only about 80% were achieved, and they were not improved by increasing the concentration of the acid or the volume of the eluting solution.

Recovery by Soxhlet Extraction

Iridium was fed onto resin beds 2 cm. deep in small columns as described above, and the beds were washed free of cerium with 20 ml. of 0.8 *M* hydrochloric acid. The upright part of the column was removed and the beds allowed to drain. The columns were then inverted and the resin bed was shoved out, along with the glass-wool supporting pad, with a stirring rod into a specially prepared glass thimble. This thimble was made by blowing a small hole in the bottom of a soft-glass test tube, cutting the tube to the appropriate length, and pulling some glass wool through the hole so that liquids would pass through but not resin particles. (The resin used in these experiments had previously been extracted to reduce color-throwing.) The thimble was placed in the small extractor and 15 ml. of 6 *M* hydrochloric acid in the pot, and the resin extracted for ½ hour.

The solutions in the pot after the extractions were pale brown in color, not as dark as chloroiridate(IV) but far from the almost colorless chloroiridate(III). These were transferred to 30-ml. beakers, evaporated to almost dryness, and analyzed for iridium with results as follows:

Number of experiments	3
Iridium taken	454 γ
Iridium recovered (range)	452–455 γ

The recovery of iridium is quantitative by this procedure. A possible explanation for the success of this operation is that the increase in temperature enhanced the reducing properties of the resin, causing reduction of the iridium most intimately bound in the resin matrix, and making it available for leaching with the hot acid solution. It is probably this iridium that cannot be reached by conventional eluants. That partial reduction had taken place was demonstrated by the restoration of the intense chloroiridate(IV) color on the addition of a few drops of 30% hydrogen peroxide solution.

Although this operation may seem rather complicated it is in reality quite simple and quick. The recovery and analysis of the iridium can easily be done in 1½ hours.

Separation and Analysis of Rhodium–Iridium Mixtures in Solution

The following procedure was successfully used to separate and analyze mixtures of rhodium and iridium in hydrochloric acid solution.

The samples were evaporated to dryness with a few milliliters of concentrated hydrochloric acid and 6 mg. of sodium chloride in 30-ml. beakers. The residues were dissolved in about 2 ml. of 0.8 *M* hydrochloric acid, and fed with a dropper onto 1.5-cm. beds of 70–100-mesh resin in small columns (which had been previously washed with 10 ml. of water and 10 ml. of the cerium(IV) solution as described above). The beakers were twice rinsed with 2 ml. of the acid solution, and the beds then eluted with 90 ml. of the cerium solution. The effluents were collected together, evaporated to a few milliliters, and analyzed for rhodium. The resin bed was extracted as described above and the recovered iridium determined.

Number of experiments	4	2
Iridium taken	454 γ	45.4 γ
Iridium recovered (range)	453–457 γ	45.0–45.2 γ
Rhodium taken	499 γ	49.9 γ
Rhodium recovered	500 γ	50.1–50.3 γ

Batch Separations of Rhodium and Iridium

An attempt to separate these two metals by stirring a solution containing them with a quantity of resin in the presence of an oxidant was not successful. Although conditions were found where no rhodium was adsorbed by the exchanger the rhodium always contained at least 10% of the iridium originally present.

The Separation of Chlororhodate and Chloroiridate(III)

Examination of the distribution coefficients (11) for the chlororhodate and chloroiridate(III) complexes indicates that a separation of these two species should be feasible on an anion exchanger with dilute hydrochloric acid solutions as eluants. A procedure of this nature would have the advantage of having the iridium on the resin in an easily eluted state.

Solutions containing approximately 500 γ of rhodium and iridium and 6 mg. of sodium chloride were evaporated to dryness. The residues were dissolved in 1 ml. of water, a few drops of a 1% solution of hydroxylammonium chloride added to reduce the quadrivalent iridium, and the solutions fed onto 3-cm. beds of <100-mesh resin in the small columns.

The rhodium complex formed a red band at the top of the bed. This band is not visible when the rhodium is fed in hydrochloric acid medium more concentrated than 0.5 *M*. The tervalent iridium band was not visible.

It was found that the rhodium could be quantitatively eluted by 80 ml. of 0.5 *M* hydrochloric acid, but that this quantity of eluant also removed significant amounts of iridium from the resin.

Elution of a bed fed with 454 γ of tervalent iridium by 100 ml. of 0.1 *M* hydrochloric acid yielded about 50 γ of iridium in the effluent. Examination of successive 10-ml. quantities of this effluent taken by a fraction collector showed that the iridium appeared shortly after the start of the elution, and that the quantity of the metal in each fraction remained almost constant at about 5 to 6 γ. This leakage of iridium could be lessened by elution with more dilute acid, but this retarded the elution of the rhodium.

It would appear that the rhodium is more strongly adsorbed than is indicated by the

distribution coefficients. Such behavior of the rhodium complex is not surprising and is in agreement with the observations of Cluett *et al.* (1), who noted that it was more difficult to remove rhodium that had been fed from a freshly prepared chlororhodate solution (which we have in this case) than from a solution that had been standing for a while.

Attempts to produce a partially hydrolyzed rhodium solution, which would have a lower affinity for the resin, by boiling, and also by adding a small quantity of urea to the solution and heating, were successful in that the ease of elution of the rhodium by 0.01 *M* hydrochloric acid was improved. However, the recoveries were still incomplete, ranging from 90% to 98% for elution with 30 ml. of the acid solution. Continued elution produced no more rhodium in the effluent. Removal of the remaining metal required an acid solution of at least 0.5 *M*. This appears to indicate that the conversion to a hydrolyzed form is not complete.

No iridium was found in the effluent on elution with 30 ml. of 0.01 *M* hydrochloric acid, but subsequent treatment with 0.5 *M* acid solution eluted small quantities of iridium.

In the face of the apparent inability to remove the rhodium without small quantities of iridium, work on this procedure was not continued.

The Separation of Partially Hydrolyzed Chlororhodate and Chloroiridate(IV)

When 5 ml. of the stock iridium solution is diluted to 100 ml. with water the resulting solution is 0.005 *M* in hydrochloric acid. It was noted that if 5 ml. of this dilute solution is fed onto a resin bed the adsorption band, while still brown in color, is not as dark as a band that is formed when the iridium is fed from a solution that has previously been boiled with hydrochloric acid or evaporated with a few milligrams of sodium chloride. Elution of the iridium adsorbed from this diluted solution with 100 ml. of 0.01 *M* hydrochloric acid produced no iridium in the effluent, but elution with 50 ml. of 6 *M* hydrochloric acid quantitatively removed the iridium.

Obviously this iridium was not in the form of chloroiridate(IV). Since the stock solution from which the diluted solution was prepared was nearly two years old, it may be assumed that the chloroiridate(IV) had undergone partial hydrolysis. Such behavior would parallel that of a chlororhodate solution (see above) except that in this case the rate of hydrolysis is probably much slower.

Repetition of this procedure with the rhodium solution showed that 25 ml. of the 0.01 *M* acid solution removed 86% to 92% of the rhodium from the resin with no more metal being removed by further elution with this solution. Removal of the rest of the rhodium could not be accomplished except under conditions which would also remove some iridium.

It was felt that if the degree of hydrolysis of the rhodium could be increased it would be possible to recover the rhodium without eluting any iridium. This was accomplished by the addition of 7 *M* ammonium hydroxide solution until a precipitate formed, and the subsequent dissolution of the precipitate with a minimum of 2 *M* hydrochloric acid. When a dilute rhodium solution was treated in this manner and fed onto a resin bed the rhodium could be completely recovered with 25 ml. of water.

Evidently this treatment produces one or more rhodium species which have no affinity for an anion exchanger. Passage of a similar solution through a cation-exchanging resin bed resulted in only partial adsorption of the rhodium, indicating that both cationic and neutral species are probably present.

Separations were carried out from the dilute, partially hydrolyzed solutions. To 5-ml. samples, each containing about 500 γ of each of the metals, were added three drops of

7 *M* ammonium hydroxide solution. The addition of the third drop produced a yellow precipitate which was redissolved by five drops of 2 *M* hydrochloric acid. The resulting solution was fed onto a 2.5-cm. resin bed of 70 to 100 mesh in a larger column, and the bed washed with 25 ml. of water followed by 50 ml. of 6 *M* hydrochloric acid. The feed and water-wash effluents were analyzed for rhodium, and the acid effluent for iridium. Quantitative separations were achieved by these means.

Unfortunately, the above separation could not be repeated when fresh rhodium and iridium solutions were used. Attempts to hydrolyze these solutions by dilution and boiling prior to the ammonia treatment resulted in maximum recoveries of 98% for rhodium and 95% for iridium. The rhodium could be completely recovered by passing the iridium fraction, after evaporation and re-treatment, through the column again. From a sample containing four times as much rhodium the same percentage loss occurred as for the smaller samples.

Although it is possible to recover all the rhodium in two stages, and presumably all the iridium by a Soxhlet extraction, the authors cannot recommend this procedure in place of the simpler and shorter method utilizing cerium(IV) described above. The one advantage of this procedure is that rhodium is produced free of other metallic elements.

By coincidence, some of this work was paralleled in the recent report by MacNevin and McKay (3), who used sodium hydroxide to precipitate the rhodium. Dissolution of this precipitate gave a solution containing almost entirely cationic rhodium, which they adsorbed on a cation exchanger to separate it from the iridium which remained in an anionic form. This reaction, like that described above, was not quantitative, and a complete separation was not achieved.

The above work demonstrates the extreme complexity of the chemistry of the platinum metals in solution, and the importance of taking into account the history of a solution sample cannot be overemphasized.

ACKNOWLEDGMENTS

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THE CHEMISTRY OF THE "AMINOCHROMES"*

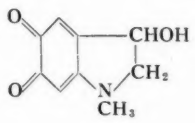
PART I. THE PREPARATION AND PAPER CHROMATOGRAPHY OF PURE ADRENOCHROME[1]

R. A. HEACOCK, C. NERENBERG, AND A. N. PAYZA

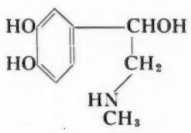
ABSTRACT

The preparation of adrenochrome in a pure stable crystalline form has been carried out by the silver oxide oxidation of adrenaline in methanol with the use of an anion-exchange resin (Dowex-1(Cl^-)) to remove heavy metal ions from the reaction mixture prior to the isolation of the product. Its paper chromatographic behavior together with that of three derivatives (adrenolutin, adrenochrome monosemicarbazone, and adrenochrome monoisonicotinic acid hydrazide) in six different solvent systems has been examined. Water was found to be the best paper chromatographic solvent so far examined for this series of compounds.

Adrenochrome (I), the substance mainly responsible for the red colors produced during the mild oxidation of adrenaline (II), was first isolated from the products of an enzymatic oxidation by Green and Richter (1). Subsequently, inorganic oxidizing agents, particularly

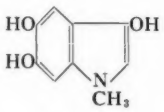


I



II

silver oxide, were successfully employed and it was observed that adrenochrome could be crystallized from methanol (containing a little formic acid) at −80° (cf. Veer (2); MacCarthy (3); Harley-Mason (4); Sobotka and Austin (5)). Green and Richter reported that adrenochrome was unstable both in the solid state and in solution (1); however, Sobotka and Austin claim that the dry crystalline material can be kept indefinitely at 0° (5). The stability of aqueous solutions of adrenochrome has been shown to be markedly affected by pH (cf. Zambotti and Moret (7)); under alkaline conditions and in the presence of certain metallic cations, particularly zinc, adrenochrome readily rearranges into adrenolutin (*N*-methyl-3,5,6-indoletriol, III) (cf. Lund (8); Fischer, Derouaux, Lambot, and Lecomte (9); Harley-Mason and Bu'Lock (10); Fischer and Lecomte (11)).



III

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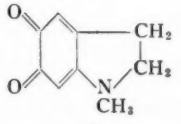
**The term "aminochromes" was suggested by Sobotka and Austin (5) for the highly colored cyclic oxidation products of β-(3,4-dihydroxyphenyl)-ethylamines and related compounds. These substances are often formulated as substituted 2,3-dihydroindole-5,6-quinones, although there is some uncertainty as to the existence of a true o-quinonoid structure (4, 6).*

Many samples of adrenochrome, prepared by existing methods, that were available to the authors appeared to contain varying amounts of adrenolutin (shown paper chromatographically by a method to be discussed later) and black water-insoluble melanin-like compounds. It appeared not improbable that contamination of the products by metal in a colloidal form or metallic ions, derived from the oxidizing agent, might be responsible for the deterioration of the samples and for the apparent instability of their aqueous solutions. In order to eliminate or drastically reduce the contamination by silver ions, the adrenaline – silver oxide reaction mixture in methanol was filtered through an anion-exchange resin bed in the chloride form prior to crystallization (at $-20°$) in order to remove ionic silver from solution as silver chloride. In this manner a highly crystalline product containing only traces of silver was obtained ($\gtrsim 0.01\%$).

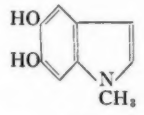
The paper chromatographic behavior of adrenochrome and related compounds has recently been studied by Fischer using *n*-butanol:acetic acid:water (8:2:2) and *i*-propanol: 0.880 ammonia:water (8:1:1) solvent systems (12). The results reported were unsatisfactory, since some of the substances apparently decomposed in these solvents. This is not altogether surprising in view of the known sensitivity of these compounds toward acids and alkalies (7, 8, 9), and furthermore Pavolini, Gambarin, and Godenigo in a study on the action of ammonia on some 5,6-indolequinones, including adrenochrome, reported a definite reaction in this case with the formation of an unstable substance, exhibiting a yellow-green fluorescence, which rapidly turns brown (13). We have repeated Fischer's work and observed with the *i*-propanol–ammonia system that the bright red non-fluorescent adrenochrome spot rapidly turned brownish-yellow in color and exhibited a yellow-green fluorescence, even on exposure to ammonia fumes, and in contact with the solvent the spot soon became dark brown indicating that marked decomposition had occurred. In the acid solvent system, a slower but definite decomposition of the adrenochrome spot was observed during the chromatography. We have found that dilute aqueous solutions of adrenochrome prepared by our method are relatively stable and that distilled water and 2% acetic acid in water are the most suitable solvents for paper chromatography. Pure adrenochrome gave a single spot $R_f 0.8 \pm 0.02$ in water on previously washed Whatman No. 1 paper. Adrenolutin had an R_f of *ca.* 0.4 under these conditions. Contamination of adrenochrome samples with adrenolutin can easily be observed paper chromatographically, since the characteristic yellow adrenolutin spot showing a strong yellow-green fluorescence is soon visible behind the red adrenochrome spot; this can be observed very quickly as it is only necessary to allow the chromatogram to run a few inches in order to see the two spots. The adrenolutin spot is quite distinct and not a diffuse "tail" to the adrenochrome spot, indicating that the impurity was present initially and not formed by continuous isomerization of the starting material. Polymeric melanin-type impurities stay in the position of the original spot. An interesting phenomenon was observed on drying of the paper chromatograms; as the paper was allowed to dry at room temperature, the color of the adrenochrome spot gradually changed from red to yellow-brown and the spot began to exhibit the characteristic adrenolutin fluorescence. The partial formation of adrenolutin was confirmed by two-dimensional chromatography, using water as running solvent in both directions, although only one spot $R_f 0.8$ was observed in the initial run; after drying and rerunning at 90° to the original direction two distinct spots with the characteristic R_f's for adrenochrome and adrenolutin appeared.

Euler, in describing the paper chromatography of adrenaline, states that after the chromatograms have been dried adrenaline spots show an apple-green fluorescence (14, p. 16). A possible explanation of this observation would be the air-oxidation of the

spot to adrenochrome followed by isomerization to adrenolutin on the paper. Therefore it would appear that a thin film of adrenochrome on paper will spontaneously rearrange into adrenolutin. This type of behavior has also been observed by Austin, Chanley, and Sobotka with the related compound epinochrome (IV), which even in the crystalline form undergoes a slow spontaneous rearrangement to 5,6-dihydroxy-*N*-methylindole (V) (15, 16). The paper chromatography of adrenochrome, adrenolutin, adrenoxyl (adrenochrome monosemicarbazone) (VI), and adrenochrome monoisonicotinic acid hydrazide



IV



V

(VII) has been studied in six different solvent systems: (*a*) water, (*b*) 2% acetic acid in water, (*c*) 75% methanol in water, (*d*) 75% ethanol in water, (*e*) *n*-butanol: acetic acid: water (8:2:2), and (*f*) *i*-propanol: 0.880 ammonia: water (8:1:1). Although all solvents proved satisfactory for either of the two derivatives, VI and VII, only (*a*) and (*b*) were suitable for adrenochrome and possibly only (*a*) for adrenolutin, since even in (*b*), (*c*), and (*d*) the fluorescence characteristics of the compound seem to be irreversibly altered.

An attempt to purify impure preparations of adrenochrome on cellulose columns using water as solvent was disappointing, since, although pure aqueous solutions of adrenochrome were probably obtained, it was not possible to crystallize the adrenochrome from water, and all samples prepared by freeze-drying under high vacuum (a technique which gave a very finely divided product) were shown chromatographically to be contaminated to some extent with adrenolutin (fortuitously formed during the drying process).

In view of the very considerable interest that has developed, in the physiological activity of adrenochrome and related compounds, in recent years (see Bacq (17) and Hoffer (18) for lists of references) the necessity for working with the compounds in a pure and stable form has become of paramount importance.

EXPERIMENTAL

Preparation of Adrenochrome

L-Adrenaline (9.15 g.) was suspended in methanol (360 ml.) and 90% formic acid added dropwise with stirring until a clear solution was obtained (*ca.* 3.5 ml.). Freshly prepared silver oxide (36.3 g.) was added portionwise during a period of 3 minutes, the reaction temperature being maintained between 18° and 23° during the addition of the oxidant. The reaction mixture was filtered (with suction) through a Dowex-1(Cl^-) (200/400 mesh) resin bed (diam. = 6.5 cm., height = 3.7 cm.)* and the deep red filtrate was allowed to crystallize slowly at −20°. Pure adrenochrome (1.6 g.) was obtained in deep-violet needles, m.p. 112° with decomposition. Found: C, 60.30; H, 4.69; N, 7.76. Calc. for $C_9H_9O_3N$: C, 60.33; H, 5.02; N, 7.81%. The ultraviolet and visible absorption spectra were measured in aqueous solution (λ_{max}: 301, 487 mμ; λ_{min}: 262, 361 mμ).

Samples of adrenochrome which we have prepared by repeating existing procedures contain, in our view, less well defined crystals than the product obtained as described above (rapid cooling to −80° tends to produce an amorphous product) and the products are

**The resin was prepared by extensive washing: (1) with 3N hydrochloric acid, (2) with water until neutral to litmus, and (3) finally with methanol until the washings were transparent to ultraviolet light.*

invariably more or less contaminated with adrenolutin and melanin. This has been demonstrated paper chromatographically (using Whatman No. 1 paper with water as running solvent). No particular advantage either in yield, purity, or crystalline form, appeared to attend the use of absolutely dry methanol. The silver contents of adrenochrome samples prepared in this manner and by the method of Sobotka and Austin (5) were determined by the dithizone method after complete oxidation of the organic material in the sample with a mixture of nitric and perchloric acids (cf. 19, p. 544) and were observed to be very low (not greater than *ca.* 100 parts per million) whereas preparations obtained by other routes had considerably higher silver contents (of the order of 1000 p.p.m.). Sobotka and Austin filtered the methanol reaction mixture through a sodium sulphate bed prior to crystallization. This may have fortuitously acted as an anion-exchange resin and removed silver ions from solution as the sulphate. It is conceivable that both the resin and the sodium sulphate beds would help to hold back colloidal as well as ionic silver. One possible advantage of the resin over sodium sulphate would be that it would enable the reaction to be carried out in aqueous solution if required.

The mother liquors were examined chromatographically on paper using water as solvent and there was evidence that they contained adrenochrome R_f 0.82, a little adrenolutin R_f 0.4–0.45, a non-fluorescent dark-violet unidentified compound R_f 0.92, and a non-fluorescent colorless zone R_f 0.0–0.4. All these zones gave blue colors (i.e. reduced) with the ferric chloride – potassium ferricyanide reagent (see next section). The low R_f area probably contained some unchanged adrenaline, since it gave a red color when sprayed with potassium ferricyanide or ammonium persulphate solution.

Paper Chromatography of Adrenochrome and Related Compounds

Whatman No. 1 paper was washed with distilled water for 12 hours and dried prior to use. It was observed that unwashed paper caused some decomposition of the adrenochrome. The ascending method for paper chromatography was invariably employed, and 10–20 μg. of sample were applied to the paper in each case. The results obtained are given in Table I.

In all cases, the solvent was allowed to ascend a distance of *ca.* 9 to 12 inches. There was a considerable variability in the time required for this to occur; water and 2% acetic acid having the advantage of giving considerably quicker results than the other solvent systems. The approximate times taken by the various solvents are given in Table II.

Detection of Spots

All four compounds are colored and therefore are self-indicating. Adrenolutin (III) also exhibits a marked yellow-green fluorescence in ultraviolet light. It has been previously stated that, on drying, the spots of I undergo a slow change to III; this substance, being a catechol derivative, has reducing properties and the chromatogram can be developed in the following manner (if a permanent record is required). The developing solution was prepared immediately before use, and consisted of 3% ferric chloride solution (5 ml.), 3% potassium ferricyanide solution (5 ml.), and water (90 ml.). The papers were dipped in the reagent and the reducing compounds formed permanent blue spots. The excess reagent was washed off; the papers were dipped in 2 *N* hydrochloric acid and finally excess acid was washed off. Other chromogenic reagents for adrenochrome include: (*a*) Ehrlich's reagent (violet spot), (*b*) 3% ferric chloride solution (gray-brown spot), (*c*) diazotized *p*-nitroaniline (red-brown spot), and (*d*) zinc chloride solution (yellow-green fluorescent spot in ultraviolet light).

TABLE I

R_f IN STATED SOLVENT SYSTEMS

Compound	A	B	C	D	E	F
Adrenochrome (I)	0.8 ±0.02	0.82±0.02	S. dec. (0.7–0.8)	S. dec. (0.7–0.8)	R. dec.¶	R. dec.
Adrenolutin (III)*	0.45±0.05	0.47±0.03§	S. dec. (0.7–0.8)	S. dec. (0.7–0.8)	R. dec.	R. dec.
Adrenoxyl (VI)†	0.48±0.05	0.50±0.03	0.65±0.05	0.85±0.05‖	0.57±0.05**	0.58±0.05**
Adrenochrome monoisonicotinic acid hydrazide (VII)‡	0.30	0.42	0.72	0.65	0.21	0.62**

NOTE.—*A = Water. B = 2% acetic acid in water. C = Methanol:water (3:1). D = Ethanol:water (3:1). E = n-Butanol:acetic acid:water (8:2:2). F = i-Propanol:0.880 ammonia:water (8:1:1). S. dec. = slow decomposition. R. dec. = rapid decomposition.*

* = *The adrenolutin was prepared by the method of Harley-Mason and Bu'Lock (20).*

† = *Supplied by the Labaz Co.*

‡ = *Supplied by the Pfizer Co.*

§ = *In all acidic solvents adrenolutin exhibited a pink fluorescence.*

‖ = *Occasionally inexplicable lower R_f's were observed for adrenoxyl with this solvent system.*

¶ = *Differing results were obtained dependent on the time taken to run the chromatogram. The red color of the spot slowly faded with the formation of a dirty yellow diffuse spot exhibiting a pink fluorescence.*

** = *These results are different from those reported previously (12); we are unable to explain these discrepancies. The R_f values quoted in Table I were obtained consistently in our investigations. Fischer's claim that adrenoxyl resolves into adrenochrome and a fluorescing spot R_f 0.88 in the ammoniacal solvent system F (12) would appear to be due to a misinterpretation of the evidence in view of known instability of adrenochrome in ammonia.*

TABLE II

Solvent system	A	B	C	D	E	F
Approximate running time (hours)	2.5–3.0	2.5–3.0	7.5	15.5–18.0	15.5–18.0	18.0–20.0

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A STUDY OF GRAFT COPOLYMERS

I. PREPARATION AND VISCOSITY BEHAVIOR[1]

J. A. MANSON[2] AND L. H. CRAGG

ABSTRACT

Graft polymers were prepared by the redox polymerization of styrene in the presence of oxidized polystyrene or copolymers of styrene and 4-vinylcyclohexene-1; the maximum number of hydroperoxide groups per thousand monomeric units in the oxidized polymers was 18. Evidence that grafting had indeed occurred was obtained from measurements of monomer disappearance, of the decrease in hydroperoxide content of the backbone polymer during reaction, and of the infrared absorption by the polymer before and after the grafting procedure.

Although the experimental results clearly support the conclusion that branching occurred, values of Huggins' k' for both unfractionated and fractionated graft polymers were no higher than for linear polystyrene ($0.39 < k' < 0.41$ in butanone). It was concluded that, though k' is sensitive to bushy branching, Huggins' k' is not measurably affected by the presence in a polymer of a few linear branches per molecule.

INTRODUCTION

The study of branching in high polymers is important to the understanding of the relationships between molecular structure and physical properties. It is all the more important because most polymers, even ones usually assumed to be linear, are branched to some extent.

Unfortunately, the determination of the extent, or degree, of branching (that is, the average number of branches per molecule) is seldom easy. The most rigorous method is based on the fact that the size, and hence intrinsic viscosity, is less for a branched molecule than for a linear molecule of the same molecular weight (26, 29). The application of this method requires the making of viscosity and light-scattering measurements, which are tedious and which require expensive equipment. Another method for the detection of branching has been based upon the determination of Huggins' k' (14), the slope constant of the curve relating reduced viscosity to concentration; a great deal of empirical evidence has been found indicating a correlation between the presence of branching in a polymer and unusually large values of k' (10, 18, 25). Since accurate viscosity measurements can be made readily with fairly simple equipment, this method would, if generally applicable, be very useful.

Since, however, no suitable comparison of these two methods had been made, it was decided to undertake a study of the relationship between Huggins' k' and the degree of branching as determined from measurements of the intrinsic viscosity and molecular weight of branched and unbranched polymers.

In this study it was desirable to have samples of a high polymer, in some of which the molecules would all be essentially linear, while in others each of the molecules would have a known number of linear side chains attached to the main chain. However, most methods available at the time for the preparation of branched polymers with fairly high molecular weights had serious drawbacks.

If one uses polymerization methods involving chain transfer (1, 3, 13), or copolymerizes

[1]*Manuscript received January 13, 1958.*

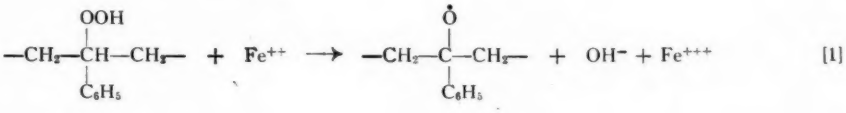
Contribution from the Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ontario, with financial assistance from the National Research Council through the Associate Committee on Synthetic Rubber Research. Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, September, 1956. Most of this work was reported at the 6th Canadian High Polymer Forum in St. Catharines, Ontario, April, 1955.

[2]*Present address: Air Reduction Company, Inc., Murray Hill, New Jersey. Holder of the R. J. Eddy Foundation Scholarship, 1953–1954.*

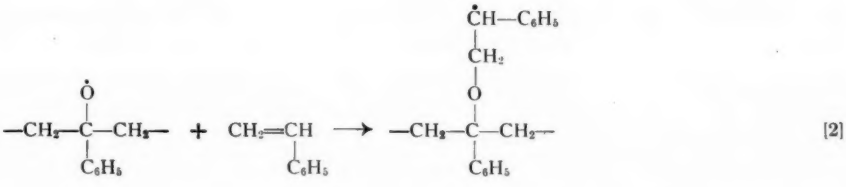
a monomer with a cross-linking agent, such as a divinyl compound (6, 28), or irradiates a partially halogenated polymer in the presence of its monomer (15, 16), one obtains a complex mixture of linear and branched polymers that is often difficult to resolve into its components. Moreover, these methods do not yield polymers with simple branches, but rather encourage the growth of branches on branches or the formation of gel.

The condensation of a monomer with a molecule having a known number of reactive functional groups was used by Schaefgen and Flory (24) to produce polymers having a known number of branches per molecule, but the average molecular weights obtained were rather low (less than 38,000) and the structure of the branched molecule was unusual (all branches radiating from a single "hub").

By contrast, the technique developed at the Polytechnic Institute of Brooklyn (21) for the grafting of side-chains onto a vinyl-type backbone seemed very attractive. In this method the hydroperoxide resulting from the oxidation of a vinyl polymer is used to initiate the polymerization of a vinyl monomer under redox conditions (see equations 1 and 2). As well as making possible the control of the degree of branching (by varying the degree of oxidation of the backbone polymer), this method should, in principle, yield a product free of linear material.



[1]



[2]

Several such graft polymerizations were carried out. The backbone polymers used were polystyrene and copolymers of styrene and 4-vinylcyclohexene-1—the latter because they were expected to oxidize more readily than styrene alone. These polymers were oxidized to varying degrees, and the products were used as initiators in the redox emulsion polymerization of styrene. Since this work was first reported at St. Catharines, Metz and Mesrobian have published a report of similar experiments (22); they were, however, unable to achieve satisfactory oxidation of polystyrene itself. Similar studies have also been described by Hahn and Lechtenböhmer (9). In neither case were measurements of Huggins' k' reported.

In this paper the preparation of the graft polymers is described and evidence that grafting did, in fact, occur is presented and discussed. Finally, measurements of intrinsic viscosity and Huggins' k' are given for the graft polymers and for their fractions.

Other more direct evidence for grafting, based on viscosity and light-scattering measurements, will be given elsewhere (19).

EXPERIMENTAL

1. *Materials*

Monomers were provided by the Polymer Corporation, Limited, Sarnia. Before use they were freed of inhibitor by washing with dilute aqueous potassium hydroxide, rinsed

with distilled water, and dried with Drierite. Cumene hydroperoxide (60%) was also provided by the Polymer Corporation. Phenyl-β-naphthylamine and benzoyl peroxide were both practical grade reagents supplied by the Eastman Kodak Company.

Polystyrene samples used for oxidation were prepared by a method described earlier (18); copolymers of styrene and 4-vinylcyclohexene-1 were prepared according to a similar recipe.

Tetralin, of Certified Chemical grade, was obtained from the British Drug Houses. Other solvents were of technical grade, and were used without further purification.

Inorganic reagents were of Analar grade, supplied by the British Drug Houses, or of equivalent quality. Nitrogen was purified by passing it first through Fieser's solution (8, p. 395) and then through a saturated solution of lead acetate.

2. Oxidations

Solutions of the backbone polymers in tetralin were oxidized at temperatures within the range 70° to 80° C.—usually at 75(±0.2)° C.— by passing oxygen through a sintered-glass bubbling tube in the solution at a rate sufficient to bring about rapid and thorough bubbling without excessive foaming. (No attempt was made to purify the oxygen or to regulate its flow precisely.)

Suitable concentrations ranged from 2 g./dl. for a high-molecular-weight polymer to 5 g./dl. for a low-molecular-weight one. In general, the oxidation was more successful with the lower-molecular-weight polymers.

After bubbling had been continued for a time estimated to correspond to the degree of oxidation desired the product was precipitated in methanol or ethanol. In order to remove tetralin (and its hydroperoxide), the gummy precipitate was reprecipitated several times from a solution in butanone before drying under reduced pressure at 45° C. to constant weight. The addition of Dry Ice to either the solution or the precipitant was found to help in obtaining a porous, easily dried material. Tests showed that with repeated precipitation the observed hydroperoxide content for the precipitated and reprecipitated polymers decreased rapidly at first, but then leveled off to an approximately constant value when a clear, porous product, free from the odor of tetralin, had been obtained.

3. Analysis for Hydroperoxide Content

Determination of the peroxide or hydroperoxide content of a high polymer is difficult (2, 27). Although iodometric methods should give values closer to absolute ones than do methods using ferrous ion, the most consistently reproducible results were obtained using the spectrophotometric procedure, based on the oxidation of ferrous ion, which was developed by Laitinen and Nelson (17). Provided that freshly prepared solutions were used, and that a calibration had been made recently, results for various samples of the same polymer were reproducible to within ±10% in most runs (or, at worst, to within ±20%).

In order to see whether or not the spectrophotometric method gave reliable absolute values for hydroperoxide content, the purity of a sample of 60% cumene hydroperoxide was determined. The average value, a mean of 13 determinations, was 108(±11)%, as compared to an average value of 62(±1)% obtained by means of a conventional iodometric titration (27, p. 53). Although cumene hydroperoxide is not necessarily a valid standard for the analysis of a high polymer, its structure is similar to that of the polymeric hydroperoxide. It is possible, then, that the values of hydroperoxide content found for the polymers studied are somewhat high.

In this paper hydroperoxide content is expressed as a "hydroperoxide number": the number of hydroperoxide groups per thousand monomeric styrene units.

4. Graft Polymerizations

Graft polymers were prepared in emulsion at 35(±0.2)° C. A typical recipe follows:

Oxidized polymer (in this example, one with a hydroperoxide number of 10)	2.0 g.
Monomer	15.0 g.
Soap flakes	5.0 g.
Water	90.0 g.
Potassium pyrophosphate	2.2 g.
Ferrous ammonium sulphate (hexahydrate)	0.2 g.

Thus, with 2.0 g. of a polymer of hydroperoxide number 10, the amounts of pyrophosphate and ferrous salts listed above were used; with a polymer of higher hydroperoxide content, proportionately larger amounts of the salts were used. If more than 15 ml. of styrene was required to dissolve the backbone polymer, proportionately more soap and water were used.

First, the backbone polymer was allowed to stand with enough styrene to effect solution. Then the required amount of water was divided into two portions—one for a soap solution, and one for a ferrous pyrophosphate solution. Both solutions were prepared by heating to 60° C.

As soon as the polymer had dissolved, the two hot solutions were swept out with purified nitrogen, combined, and placed with the polymer solution in a 250 ml. bottle fitted with a self-sealing cap. After the contents had been swept out again with nitrogen, the bottles were capped and, by means of a syringe, charged with nitrogen at a pressure of 10 to 15 p.s.i. The bottles were shaken vigorously in order to ensure emulsification, placed in a rack held in a constant-temperature bath, and rotated end-over-end at 33 r.p.m.

When desired, aliquot samples were withdrawn by syringe, and the polymer in them precipitated in methanol containing 0.1% hydroquinone; the percentage conversion was determined from the dry weight of the precipitated polymer. When the polymerization was judged to have proceeded to the desired degree of conversion, the contents of the bottles were poured into methanol–hydroquinone solution. After it was aged overnight, the precipitated polymer was washed with hot distilled water, rinsed three times with methanol, and dried at 45° C. under reduced pressure to constant weight.

5. Infrared Spectra

Infrared spectra were determined with a Perkin-Elmer recording spectrophotometer, Model 21. Solutions in chloroform of two graft polymers, GC-211 and GC-220, and of two blanks, GC-320 and GC-321 (prepared just as the graft polymers were, except that unoxidized polystyrene was used in place of oxidized polystyrene), were examined in calcium fluoride cells throughout the range 1200–3800 $cm.^{-1}$. Spectra for films of samples GC-210, GC-220, GC-250, and GC-320 were obtained independently in the laboratories of the Polymer Corporation, Limited.

6. Fractionation

The primary fractionation of a graft polymer was achieved by fractional precipitation, at 45° C., from a solution in butanone or in a butanone–benzene mixture, by the progressive addition of methanol or a methanol–butanone mixture. The fractions taken weighed not more than one-fourth of the original weight of the polymer fractionated, and with each polymer the fractionation was continued until at least three-fourths of the polymer had been precipitated.

After each swollen precipitate had been separated, it was carefully washed with a

small portion of solvent, and reprecipitated from a solution in butanone. The fibrous product was recovered by filtration, washed with methanol, and dried under reduced pressure at 45° C. to constant weight.

7. Viscosity Measurements

Values of intrinsic viscosity, $[\eta]$, were, unless otherwise noted, determined as described previously (18), by means of the equation of Mead and Fuoss (20):

$$(\ln \eta_r)/c = [\eta] - \beta[\eta]^2 c. \qquad [3]$$

Values of $(\ln t_r)/c$ (where t_r = flow time of solution/flow time of solvent) were determined and plotted against concentration; since Ubbelohde viscometers having negligible kinetic energy corrections were used (7), $(\ln t_r)/c$ is equivalent to $(\ln \eta_r)/c$. Values of k', the slope constant of the Huggins' equation,

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c, \qquad [4]$$

were computed from the relation $k' + \beta = 0.50$.

RESULTS AND DISCUSSION

1. Oxidations

In Fig. 1 are presented some typical results showing the effect of duration of the period of oxidation on the hydroperoxide content of low-molecular-weight polymers ($0.5 < [\eta]$ in butanone < 0.8). Lengths of the vertical lines represent approximately the error in the determination of hydroperoxide number. Although the points are rather scattered, partly because of variations in the rate of flow of oxygen, the data show that the maximum hydroperoxide content was usually reached after oxidation had proceeded for 8–12 hours.

In order to find out whether degradation had occurred during oxidation, the intrinsic

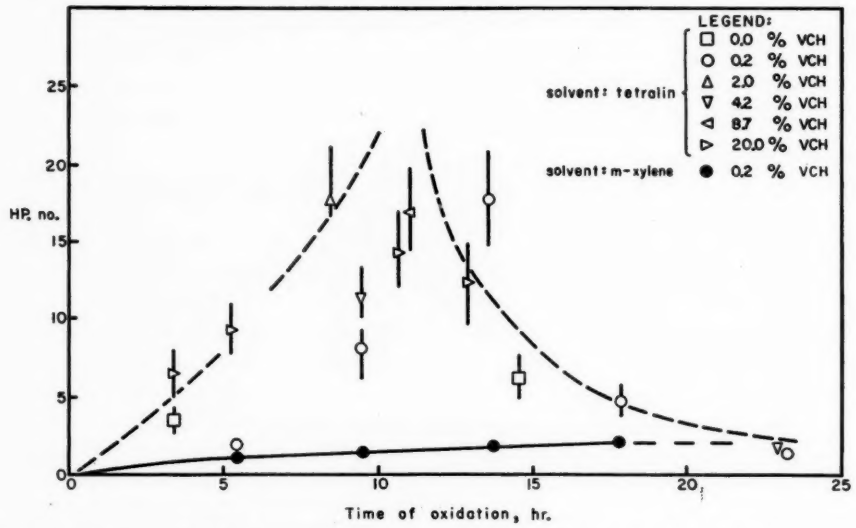


FIG. 1. Dependence of hydroperoxide content on time of oxidation and on 4-vinylcyclohexene-1 (VCH) content.

viscosities of several polymers were determined before and after oxidation. No decrease in intrinsic viscosity was observed, and it was concluded that degradation had not occurred.

The data in Fig. 1 confirm the importance of the solvent to the oxidation (22). While relatively high hydroperoxide contents were obtained for polymers oxidized in tetralin (which is itself readily oxidized to its hydroperoxide under the conditions used here), hydroperoxide numbers for polymers oxidized in *m*-xylene were very close to those found for unoxidized polymers.[3]

It is also clear that pure polystyrene is not readily oxidized by molecular oxygen (9); the highest hydroperoxide number obtained was 9, corresponding to a hydroperoxide concentration of about one mole per cent.

In the hope of obtaining higher hydroperoxide numbers, several modifications of the procedure were tried:

1. The use of copolymers of styrene and 4-vinylcyclohexene-1, the oxidation of which should be unaffected by the steric effects encountered with pure polystyrene (22).
2. The use of partially isopropylated polystyrene.
3. The use of catalysts, such as benzoyl peroxide or cumene hydroperoxide.

However, none of these modified procedures gave values of hydroperoxide content greater than 18. Although this value, the highest observed, was obtained with a styrene-vinylcyclohexene copolymer, no correlation was found between hydroperoxide number and vinylcyclohexene content.

2. Evidence for Grafting

(a) Conversion Studies

Proof that the polymeric hydroperoxides initiated the rapid polymerization of styrene was obtained from measurements of the percentage conversion of styrene to polymer as a function of time. Conversion data for a typical graft polymerization, GC-140, are given in Fig. 2; for comparison, data are included for a blank polymerization, GC-141,

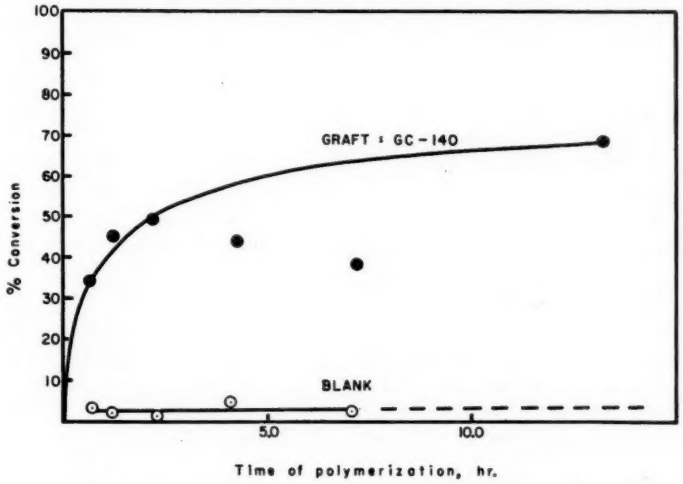


FIG. 2. Dependence of percentage conversion on time for a graft and a blank polymerization. ● Graft. ○ Blank.

[3]*As mentioned above, care was taken to remove residual tetralin from the oxidized polymers.*

a duplicate of GC-140, except for the omission of oxidized polymer from the polymerization recipe. After 1 hour of reaction, only a small amount (<3%) of the initial styrene had been polymerized in the blank, whereas in the same period more than half of the initial styrene in the graft polymerization had been polymerized.

As the polymerization proceeded, the conversion data tended to become scattered, probably because the emulsion had usually broken within the first three hours and it was consequently impossible to take truly representative samples. However, the value of percentage conversion for the total polymer (corresponding to the last point in the curve for GC-140) always fitted in well with values found for aliquot samples taken during the early stages of polymerization.

Further evidence for the initiation of polymerization by the polymeric hydroperoxides is given in Tables I and II, in which are summarized polymerization and conversion data for several series of graft polymers, and for a number of "blank" polymers prepared (with one exception, GC-141) by replacing oxidized polymer with ordinary polymer.

Without exception, a larger proportion—usually a much larger proportion—of the styrene was polymerized with oxidized than with ordinary polymer. (The relatively

TABLE I

VISCOSITY AND CONVERSION DATA FOR GRAFT POLYMERS

Sample	% VCH* in backbone	HP no. of backbone polymer	Weight, g., backbone of polymer	Weight, g., of styrene	Polymerization time, hours	Percentage conversion	[η] in benzene, dl./g. Backbone polymer	[η] in benzene, dl./g. Graft polymer
GC-100	0.8	9.5	1.5	10.2	10.0	50	1.70	7.55
GC-110	10.0	18	0.7	14.0	10.0	50	1.13	4.85
GC-140	8.3	7.7	2.0	22.7	13.5	50	1.20	6.54
GC-161	0.0	1.8	1.0	10.2	—	10	—	—
GC-162	0.0	1.8	1.0	10.2	—	10	—	—
GC-163	0.0	1.8	1.0	10.2	—	10	—	—
GC-180	10.0	1.9	1.0	22.7	8.0	10	0.92†	0.95
GC-190	0.4	3.0	1.0	16.4	11.0	10	0.78	2.96
GC-200	0.2	2.0	1.0	11.4	11.0	10	0.82	3.05
GC-210	20.0	9.0	1.0	13.6	9.0	36	0.85†	5.44
GC-211	20.0	9.0	1.0	15.0	0.5	82	0.85†	6.43
GC-220	10.0	16	1.0	13.6	9.0	38	0.92†	5.08
GC-230	0.4	7.0	1.0	18.2	9.0	40	3.90	6.05
GC-240	0.4	14	1.0	18.2	9.0	40	3.79	6.19
GC-241	0.4	14	1.0	18.2	1 0	13	3.79	4.19
GC-621	0.0	6.6	0.5	9.1	6.0	15	2.23	6.59

**4-Vinylcyclohexene-1.*
†*Calculated from value in butanone using relationship given in Reference 18.*

TABLE II

VISCOSITY AND CONVERSION DATA FOR BLANK POLYMERS

Sample	Weight, g. Polymer	Weight, g. Styrene	Polymerization time, hours	Percentage conversion	[η] in benzene, dl./g. Backbone polymer	[η] in benzene, dl./g. Product
GC-141*	—	22.7	13.5	2.5	—	3.40
GC-250	1.0	18.2	6.0	2.8	1.58	2.38
GC-320	1.0	9.1	5.0	5.6	0.92	1.03
GC-321	1.0	9.1	5.0	2.2	0.92	1.03
GC-322	1.0	9.1	5.0	2.2	0.92	1.02
GC-323	1.0	9.1	5.0	3.3	0.92	1.02

**This sample was prepared using the same recipe as for GC-140, except that oxidized polymer was omitted.*

low conversions in polymerizations GC-161 to GC-200 may be due to the low hydroperoxide content of the backbone polymers used in these runs, but, in general, no close relationship between percentage conversion and hydroperoxide content is evident.) These data also indicate no correlation between the vinylcyclohexene content of the backbone polymer and the percentage conversion.

(*b*) *Disappearance of Hydroperoxide Groups*

The evidence just cited indicates that, under the conditions of our grafting experiments, the formation of polymer is initiated by the hydroperoxide groups in the parent (or backbone) polymer. Other evidence of this was obtained from measurements of hydroperoxide content before and after polymerization. Results of such measurements are assembled in Table III. The formation of new polymer in the presence of the parent

TABLE III

DECREASE IN HYDROPEROXIDE CONTENT DURING GRAFTING

Sample	HP no. of backbone polymer	HP no. of graft polymer	
		Calculated*	Observed
GC-100	9.5	2.5	(2.0)†
GC-110	18.4	3.7	0.60
GC-140	7.7	1.4	0.33
GC-180	1.9	0.97	0.86
GC-190	3.0	1.5	1.1
GC-200	2.0	1.2	0.77
GC-210	9.0	2.4	0.57
GC-211	9.0	1.1	0.97
GC-220	16.0	3.4	0.64
GC-230	7.0	1.7	0.27
GC-240	14.0	2.6	0.42
GC-241	14.0	4.4	(3.6)†

**Calculated on the assumption that none of the polymeric hydroperoxide groups disappear during polymerization.*

†*Appears to be anomalous.*

polymer must yield a product whose hydroperoxide number (the number of hydroperoxide groups per thousand monomer units) is less than that of the parent polymer. This would be true regardless of whether or not the new polymer is attached to the old. If none of the hydroperoxide groups on the backbone chain were used up in initiating new polymer growth, the hydroperoxide number of the product would still be less because the number of monomer units in the polymer would be increased. In column 3 are listed the values of hydroperoxide number calculated on the assumption that the decrease is merely due to this "dilution" effect;[4] in column 4 are the values actually observed. Even after allowance is made for the rather imprecise results obtained in these analyses, it is clear that hydroperoxide groups do disappear in these graft polymerizations. The precautions taken to remove residual tetralin hydroperoxide were such that at worst the contribution of tetralin hydroperoxide to the hydroperoxide number of the backbone

[4]*The following expression was used for the calculation:*

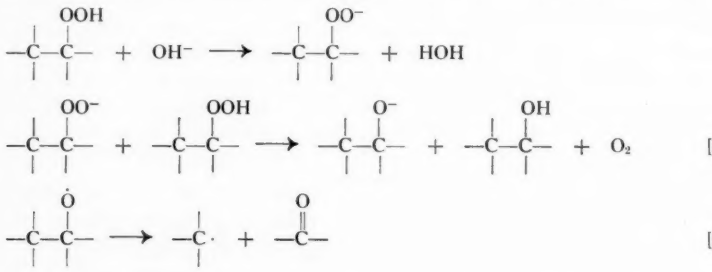
$$\frac{\text{wt.}_{bb} \times \text{hydroperoxide no.}_{bb} + \text{wt.}_{ps} \times 0.50}{\text{wt. graft polymer}}$$

where the subscripts bb *and* ps *refer to backbone polymer and polymerized styrene, respectively. For convenience, it is assumed that the hydroperoxide number of the polymerized styrene is 0.50, a reasonable value slightly lower than the average of 0.55 found for the blanks GC-320, GC-321, GC-322, and GC-323; choice of an even lower value would not affect the conclusions.*

polymer would be less than 1. The polymerization must, therefore, have occurred mainly at the polymeric hydroperoxide sites.

(*c*) *Absence of Side Reactions*

So far in this discussion it has been assumed that in the presence of an excess of monomer a polymeric hydroperoxide group disappears by the series of reactions outlined in equations [1] and [2], rather than by such polar or radical side reactions as the following:



[5]

[6]

The occurrence of reactions represented by equations [5] and [6] would result in the disappearance of hydroperoxide groups, and, in the case of the free-radical reaction, in the formation of free radicals that would initiate the formation of linear polymer. Experimental evidence for the occurrence of these side reactions was sought, but in vain.

That a polar decomposition induced by the alkaline nature of the emulsion did not occur was demonstrated in the following way. Emulsions of two different polymeric hydroperoxides were prepared, following the recipe for graft polymerizations in all respects except that the ferrous salt was omitted, and these emulsions were rotated in the constant-temperature bath for 1.5 hours and 1.0 hour, respectively—times sufficient in a graft polymerization for the conversion of most of the monomer to polymer. The resulting change in hydroperoxide number was negligible: from 4.9 to 4.6 and from 5.2 to 5.6, respectively. It was concluded that the polymeric hydroperoxides used in this study were stable at the pH existing in the emulsions.

The reaction represented by equation [6] would result in the formation of terminal carbonyl groups. The infrared spectra for graft polymers GC-211 and GC-220 and for blanks GC-320 and GC-321 were carefully examined for the presence of absorption peaks corresponding to the absorption frequency of the carbonyl group (in the range 1720–1730 cm.$^{-1}$). Although the carbonyl group is detectable at low concentrations (23), no such peaks were found. The spectra for the graft polymers were in fact identical in this range with those for the blanks. These findings were confirmed by examination of the spectra for films prepared from the graft polymers GC-210 and GC-220, and from blanks GC-250 and GC-320.

These findings, though negative, constitute additional justification for our assumption that, under the conditions of our grafting experiments, hydroperoxide radicals on the parent polymer molecules initiate the growth of polymer branches.

(*d*) *Fractionation Behavior*

Finally, it should be pointed out that the fractionation behavior of the graft polymers also indicates that grafting has occurred. In carrying out a primary fractionation of linear polystyrene, it is relatively easy to control the number and size of the fractions. With the graft polymers, however, this was very difficult; once precipitation began, a very slight excess of non-solvent tended to bring down all or most of the polymer. This

is the behavior to be expected if the polymer molecules are all large and branched (as they would be if the polymer chains formed were all attached to a pre-existing backbone chain). It is not the behavior to be expected if the new polymer chains were independent molecules, for then there would be the usual wide distribution of molecular weights, and the usual wide differences in solubility.

All of this evidence is consistent with only one conclusion: that in the polymerizations described in this paper grafting had occurred, that is, branched polystyrene molecules had been formed by the growth of polystyrene chains onto a polystyrene backbone chain.

3. Viscosity Results

If every, or almost every, hydroperoxide group in the backbone polymer became a point of attachment for a branch, the graft polymer molecules must have been fairly extensively branched. For example, molecules of the backbone polymer for the graft polymer GC-210 (Table I) contained, on the average, nine hydroperoxide groups per 1000 monomer units, and hence an average molecule of the graft polymer may have had as many as nine branches per 1000 monomeric units in the backbone chain (i.e., 9×DP/1000 branches, where DP is the degree of polymerization of the parent polymer).

It was expected, therefore, that Huggins' k' would have higher values for the graft polymers than for linear polystyrene. The experimental values did not, however, show this difference. In the (unfractionated) graft polymers they fell within the range characteristic of linear polystyrene (0.39–0.44 in butanone, 0.37–0.39 in benzene), and the averages of the values obtained with fractions also fell within these ranges (see Reference 19, Table IV).

Evidently k' is not measurably affected by the branching present in these polymers. This was an unexpected finding. Even a very little (i.e., 0.01%) divinylbenzene copolymerized with styrene was found to produce sufficient non-linearity in the polymer to increase k' appreciably (6, 19). Indeed, a great deal of evidence has been accumulated for many different polymers showing that non-linearity in polymers leads to high values of k'.

A careful re-examination of this evidence discloses, however, that when these increases have been observed the non-linearity of the polymer was due either to a small degree of cross-linking or to branching resulting from reactions which could have led (and probably had led) to branches that were themselves branched. Schaefgen and Flory (24) have indeed reported a very slight increase in k' for a branched condensation polymer prepared in such a way as to preclude branched branches, but in view of the errors involved in the determination of k' it is questionable whether the increase observed (average value of k' for linear polymer, 0.36, for polymer with eight branches, 0.38) is significant.

On the basis of the evidence now available, it may be concluded that k' is affected more by bushy branching than by simple branching. Indeed, it may well be that measurements of k' could afford a means of distinguishing between different types of branching.

This conclusion seems to be reasonable, for k' is a function of the segment density in the molecular coil (4), and at the same temperature and in the same solvent, the segment density for a molecule consisting of a backbone carrying a few long branches should be significantly less than that for a bushy molecule, and probably little different from that for a linear molecule of the same weight.

It would seem, then, that what affects k' is not branching per se but branching of such a type and to such a degree that the segment density in the molecular coil is significantly altered. Multiple branching (either of the bushy type or of the loose network type) is the kind most likely to increase the segment density. But if the considerable degree

of linear branching characteristic of our graft polymers does not affect k', it is to be expected that a small degree of multiple branching will not affect it. It is probably for this reason that, to cite two examples, Cragg and Brown (5) found k' to be normal for low-conversion GR-S, and Hobbs *et al.* (11, 12) found that a high-molecular-weight sample of polyvinyl acetate known to be branched (and probably with bushy branches) gave normal k' values.[5]

ACKNOWLEDGMENTS

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[5]*It has recently been reported (11) that branching may be detected, by a change in the slope of η_{sp}/c vs. c curves, when the change in k' is too small to be detected with certainty. When this method was applied to our graft polymers, an increase in slopes (over that obtained with linear polystyrene of the same intrinsic viscosity) was noted in the curves obtained with benzene solutions but not in those obtained with butanone solutions.*

LIGHT-ABSORPTION STUDIES

PART X. ULTRAVIOLET SPECTRA IN ACID AND BASIC MEDIA—SOME FURTHER OBSERVATIONS ON THE ORTHO EFFECT[1]

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ABSTRACT

The spectra of acetophenones and related compounds are obtained in acid and basic solution and are compared with previously reported spectra of substituted benzene derivatives. Evidence is adduced that the B-bands, not only in neutral solution, but also in acid or basic solution, are determined primarily by steric and mesomeric interactions.

Following previous work, the main cause of the ortho effect in the B-band of electronic spectra is ascribed to steric interactions between the vicinal substituents, and in this way, steric interactions explain the frequent similarity in the spectra of meta and ortho isomers. Other factors also play a part, and one of these, a short-range interaction between the substituent and the benzene ring, is discussed.

INTRODUCTION

In Part III (1) of this series it was stated that the B-band of orthodisubstituted benzene derivatives in neutral solution would be approximately the same as the B-band of para isomers, except for steric inhibition of resonance. This statement was based on the assumption that in the B-band the so-called mesomeric (resonance) interactions are of greater importance than inductive-type interactions. The effects of mesomeric interaction in spectra were also developed in previous papers (2, 3, 4).

The purpose of the present communication is to extend these hypotheses to spectra in acid and alkaline solution. The spectra under these conditions frequently exhibit pronounced similarity for the ortho and meta isomers. This has been noted by Doub and Vandenbelt (5), and has also received a quantum-mechanical interpretation by Förster (6). The latter interpretation, however, is inadequate for many of the compounds under investigation. It will be shown that an equally satisfactory explanation can be obtained by assuming approximate identity of the resonance interactions in ortho and para isomers in the absence of steric and other interfering interactions. The similarity of the spectra of ortho and meta isomers may then be related to the observation that frequently both spectra resemble that of one of the monosubstituted parent compounds. In this way, the frequently observed identity in monosubstituted parent compounds and ortho and meta isomers is explained, since in the meta isomer no interaction between the two substituents occurs because of the absence of suitable resonance forms; in the ortho isomer such resonance interaction is prevented because of steric interaction between the vicinal substituents.

ULTRAVIOLET ABSORPTION SPECTRA IN ACID AND BASIC MEDIA

Table I shows spectra of benzene derivatives in acid and basic media compared with the same spectra in neutral, aqueous solution. Both B- and C-bands are listed but the discussion will be limited to B-bands. This follows, because although B- and C-bands both provide a potential measure of interaction between two or more substituents in benzene derivatives, the C-band is dependent on the B-band (3) and hence less easily related

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directly to electronic interactions. The limited data available in Table I listing both B- and C-bands confirm the suggestion made in Part VIII (3) that both bands are of similar character, since comparable wavelength displacements are again observed on changing the hydrogen-ion concentration of the solvent.

TABLE I

EFFECT OF ACIDITY AND BASICITY ON SPECTRA OF BENZENE DERIVATIVES
(Values in italics represent inflections in this and subsequent tables.)

Compound	Neutral solvent		Acid (0.1 *N* HCl) solvent		Base (*N* NaOH) solvent	
	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
Toluene (B-band)	206	6000	206	6500		
Toluene (C-band)	260	300	260	290	260	280
Diphenyl	247	16600	247	16600	247	17700
Acetophenone (B-band)	244	12000	244	12000	244	11500
Acetophenone (C-band)	276–278	1250	277	1250	277	1250
Benzaldehyde (B-band)	248	12000	249	13500	248	10000
Benzaldehyde (C-band)	279	1400	280	1500	*279*	*1200*
Nitrobenzene	266	7800	266	7800	266	6900
Benzoic acid (B-band)	226	9500	229.5	11500	223.5	9000
Benzoic acid (C-band)	270.5	850	272	1000	267	600
Phenol (B-band)	210	6000	210	6000	234	10500
Phenol (C-band)	268	1500	268	1600	285	2700
Anisole (B-band)	217	4300	217	4900	221	3600
Anisole (C-band)	*ca.261* 267 273	*1200* 1600 1300	267 272	1700 1400	267 273	1700 1400
Aniline (B-band)	230	8000	203	7500	230	8400
Aniline (C-band)	278	1400	253	170	279	1400
p-Nitrobenzoic acid	271	10000	263.5	12500	272	10600
m-Nitrobenzoic acid	265	7000	261	7100	266	7350
o-Nitrobenzoic acid	*ca.*266	5300	*ca.*262.5	5500	267	5500
p-Aminoacetophenone	308-309	16500	*ca.*260	6000	308–309	11000
m-Aminoacetophenone	*ca.*255	3500	238	12000	*ca.*255	3500
p-Hydroxybenzoic acid*	251	12500	255	13900	280	16300
m-Hydroxybenzoic acid*	*232*	*6400*	236.5	7500	*245*	*7000*
p-Nitrophenol	313–314	9500	317.5	10000*	402.5	19200*
m-Nitrophenol	272	6000	273.5	6000*	291	4500*
p-Nitroaniline	373–377	13000	372	5600*	373–379	13000
m-Nitroaniline	278–279	4500	256	7500	278–279	4650

**See Table III and Refs. 5 and 7.*

In discussing these spectra it should first be noted that numerous "exceptional" changes occur. These exceptions may be defined as effects where the acidity or basicity causes a fundamental change in the molecular entity. Thus, the removal from the conjugated system of the unshared electron pair in the amino group by the addition of acid, and the presence of base replacing either the OH group by an ONa group or the COOH by a COONa group, represent examples of this type of change.

Similarly, the effect of acid on benzoic acid spectra is to cause a change in the molecular species present, since the equilibrium

$$C_6H_5COOH \text{ hydrate} + H_2O \rightleftharpoons C_6H_5COO^- \text{ hydrate} + H_3O^+$$

will occur in aqueous solution (cf. 8), whereas in acid media the benzoate-ion concentration will be negligible. An analogous difficulty arises in the study of benzoic acid spectra in sulphuric acid, where again the molecular entities are altered to give rise to completely ionized acids $R.CO_2H_2^+$ (cf. 9). Likewise, the actual molecular species of carbonyl compounds in concentrated sulphuric acid will be predominantly $>C{=}OH^+$, again different

from the species present in neutral solution (cf. 10). Since, when the acidity of the solvent is changed, some changes in the molecular species occur almost invariably, it is difficult to determine the effect of acidity on a single molecular species.

On the other hand, it seems incorrect to neglect completely the effects of acid or base, *qua* acid or base (for instance, the effect of a changed dielectric constant), on absorption curves of a single molecular entity. That is, although the presence of a proton, for example, may lead to a complete change in the electronic structure of the molecule, sometimes this addition will merely cause a small change in the coulomb or resonance integral of the relevant atoms. This appears to be borne out by the observation of Nagakura *et al.* (10) that absorption curves of acetone in sulphuric acid media at higher acid concentrations do not cross at the isosbestic point.

This inherent effect of acid or base, apart from the frequent ability of acid or base to change the molecular species present, usually represents a *minor* effect in electronic absorption spectra. This is illustrated in Table I by a number of spectra. For instance, the addition of dilute acid or base to aqueous solutions of diphenyl, benzaldehyde, acetophenone, or nitrobenzene, or the addition of dilute acid to aqueous solutions of phenol, does not, apparently, alter the characteristic spectra to any appreciable extent. A slight change, which is evident in Table I for the above-mentioned compounds, is a small variation in the absorption intensity as measured by the molecular extinction coefficients (ϵ). These ϵ values may show either an increase or a decrease. This change, in turn, may be related to small changes in the force constants of the central linkages, a change which has previously been shown (11) to give rise mainly to intensity changes.

Further, there appears to be some evidence that this effect is transmitted preferentially across the ends of a conjugated system particularly if mesomeric or resonance interaction is appreciable. Then this interaction may cause appreciable spectral changes. For example, the spectra of *p*-aminoacetophenone, *p*-hydroxybenzoic acid, and *p*-nitrophenol, when the pH is changed, are altered to a greater extent and differently than the spectrum of either of the two monosubstituted parent compounds with similar pH changes. A similar enhanced effect is not always observed for the corresponding meta isomers (see Table I), and it may also be noted from Lemon's data (12) that spectral changes due to alkalinity in the B-band are much more pronounced in the para isomer of *p*-hydroxybenzaldehyde than in the ortho or meta isomers.

STERIC EFFECTS IN ACID AND BASIC MEDIA

A number of spectra in sulphuric acid media have already been determined (see Part VIII (3), Table II), and it was then noted that in this medium a bathochromic shift is generally observed in both B- and C-bands, compared with the spectra in neutral solution. Such a bathochromic shift would be anticipated on theoretical grounds, since generally the more ready formation of dipolar forms, because of the greater polarity of the solvent, would be more important in the electronic excited state than in the ground state.

The sulphuric acid data also indicate that the steric effect of ortho substituents in the B-band is apparently more pronounced in acidic than in neutral solution. For example, *o*-methylbenzaldehyde compared with *p*-methylbenzaldehyde in hexane solution does not show a wavelength shift in the B-band and the intensity ratio is 0.87, while in sulphuric acid solution for the same pairs of compounds a wavelength shift of 15 mμ is observed and the intensity ratio is 0.74 (3). For *o*-methyl- and *p*-methyl-acetophenone in ethanolic solution the wavelength shift for the B-band is 10 mμ, whereas in sulphuric acid solution the wavelength shift is 16 mμ. For *o*-chloro- and *p*-chloro-benzoic acid in ethanolic

solution the wavelength shift in the B-band is 5 mμ (3), whereas in dilute acid solution the wavelength shift is 12 mμ (7). These and other examples may be rationalized by supposing that the increased polarity of the solvent will often tend to keep the molecule planar, and incidentally will more effectively dislodge a less firmly held substituent in the ortho position. In this way a methyl substituent, for example in *o*-methylacetophenone, which is held in the plane of π–π conjugation by π–σ interaction, is more readily bent in sulphuric acid solution than in ethanolic solution, presumably because π–σ conjugation, compared with π–π interaction, is less effectively strengthened by the increased polarity.

This explanation shows why steric inhibition of resonance is frequently apparently more enhanced in acid media. An additional, not unrelated, effect may also be noted. If inhibition of resonance is often more at the expense of the weaker electronic interaction, the spectra of orthodisubstituted compounds in acid media would frequently be expected to resemble that of one of the monosubstituted parent compounds. In other words, steric interactions in acid solution are more likely to cause steric effects in which conjugation is sufficiently inhibited for the molecule to absorb as two distinct entities.

Further, it may be deduced from this hypothesis that ortho and meta isomers almost invariably afford similar spectra, particularly in acid or basic media. This important observation has already been noted, and has been extremely well documented by Doub and Vandenbelt (5). On the basis of simple resonance theory and our general theory of steric inhibition of resonance (1) this ortho–meta similarity may be rationalized. This follows because in meta isomers primary resonance (mesomeric) interaction is ruled out; in ortho isomers, this same mesomeric interaction is often also ruled out because of steric interaction between the two vicinal atoms or groups (see previous paragraph). Since the B- and C-bands are determined primarily by steric and mesomeric interactions, ortho and meta isomers would be expected to be similar and an enhanced similarity would be anticipated in acid and basic media. This is in fact observed. A corollary of this hypothesis would be that for such examples of ortho–meta similarity both spectra should also resemble the spectrum of one of the monosubstituted parent compounds, except that the second substituent may exert a secondary short-range effect of the type mentioned in a previous paper (11). Some relevant examples are collected in Table II, which lists spectra of ortho- and meta-disubstituted compounds together with suitable reference compounds, and also records the wavelength displacements due to the above-mentioned short-range interaction. This latter interaction will be discussed again in the next section.

The examples chosen in Table II represent groups of spectra determined under similar conditions whenever possible. Quite frequently, however, the values in a particular group represent data obtained by different workers using a variety of instruments. Even then, the data not only show a pronounced similarity in the ortho and meta isomers, but frequently also show a similarity for the above-mentioned short-range interaction. Thus, for example, in six different hydroxysubstituted compounds the wavelength shift due to the OH group is 7 ± 1.5 mμ. Likewise, for six different methylsubstituted compounds the shift due to the methyl group is 5.5 ± 1.5 mμ (see Table II). The value for the methyl group may also be compared with the well-known observation that a methyl group usually gives rise to a bathochromic shift of about 5 mμ in a variety of ethylenic systems (14). Similar sets of values may also be obtained for other substituents, for example the values for chlorine in Table II, but for many substituents the agreement is not good, particularly if the substituent is large. Some of these data will be discussed separately elsewhere (15).

In determining the wavelength shift, because of the additional effect of the secondary substituent, the meta isomer has been used, since in the ortho isomer intramolecular

TABLE II

ABSORPTION SPECTRA OF SOME DISUBSTITUTED BENZENE DERIVATIVES AND OF THE CORRESPONDING MONOSUBSTITUTED REFERENCE COMPOUNDS

Compound	Solvent	B-band		Wavelength shift (disubstituted–monosubstituted) due to second substituent (in brackets), mμ
		λ_{max}, mμ	ϵ_{max}	
o-Methylbenzonitrile*	H_2O	228.5	11100	
m-Methylbenzonitrile*	H_2O	229.5	11000	5.5 (Me-)
Benzonitrile†	H_2O	224	13000	
o-Nitrotoluene*	H_2O	266	5300	
m-Nitrotoluene*	H_2O	273	7300	4.5 (Me-)
Nitrobenzene†	H_2O	268.5	7800	
o-Xylene*	H_2O	*210*	*8300*	
m-Xylene*	H_2O	*212*	*7200*	6 (Me-)
Toluene§	H_2O	206	6000	
o-Toluic acid‡	95% Ethanol	228	5000	
m-Toluic acid§	95% Ethanol	232	9000	6 (Me-)
Benzoic acid§	H_2O	226	9500	
o-Methylacetophenone§	Conc. H_2SO_4	293	14000	
m-Methylacetophenone§	Conc. H_2SO_4	300	21000	7 (Me-)
Acetophenone§	Conc. H_2SO_4	293	20000	
o-Toluic acid§	Conc. H_2SO_4	264	16000	
m-Toluic acid§	Conc. H_2SO_4	265	16400	5 (Me-)
Benzoic acid§	Conc. H_2SO_4	260	15500	
o-Chlorobenzoic acid*	pH 3	229	5900	
m-Chlorobenzoic acid*	pH 3	231.5	9100	2 (Cl-)
Benzoic acid§	0.1 *N* HCl	229.5	11500	
o-Chlorobenzoic acid*	0.1 *N* NaOH	Indistinct band		
m-Chlorobenzoic acid*	0.1 *N* NaOH	*228*	*6900*	4.5 (Cl-)
Benzoic acid§	*N* NaOH	223.5	9000	
o-Chloronitrobenzene*	H_2O	260	4000	
m-Chloronitrobenzene*	H_2O	264	7100	-4.5 (Cl-)
Nitrobenzene†	H_2O	268.5	7800	
o-Chloroacetophenone‡	H_2O	243	6200	
m-Chloroacetophenone‡	H_2O	245	10600	1 (Cl-)
Acetophenone§	H_2O	244	12000	
o-Chlorobenzaldehyde‡	H_2O	253	10000	
m-Chlorobenzaldehyde‡	H_2O	248.5	10800	0.5 (Cl-)
Benzaldehyde§	H_2O	248	12000	
Salicylic acid*	pH 3	237	9000	
m-Hydrobenzoic acid*	pH 3	236.5	7500	7 (OH-)
Benzoic acid§	0.1 *N* HCl	229.5	11500	
Salicylic acid*	pH 9	230.5	7200	
m-Hydroxybenzoic acid*	pH 9	*232.5*	*6400*	8.5 (OH-)
Benzoic acid§	*N* NaOH	223.5	9000	
o-Hydroxyacetophenone*	0.1 *N* HCl	252.5	10900	
m-Hydroxyacetophenone*	0.1 *N* HCl	250.5	9100	6.5 (OH-)
Acetophenone§	0.1 *N* HCl	244	12000	
o-Hydroxybenzaldehyde*	0.1 *N* HCl	256	12600	
m-Hydroxybenzaldehyde*	0.1 *N* HCl	254.5	10100	5.5 (OH-)
Benzaldehyde§	0.1 *N* HCl	249	13500	
o-Nitrophenol*	pH 3	278.5	6600	
m-Nitrophenol*	pH 3	273.5	6000	7.5 (OH-)
Nitrobenzene§	0.1 *N* HCl	266	7800	
o-Dihydroxybenzene*	pH 3	*214*	*6300*	
m-Dihydroxybenzene*	pH 3	*216*	*6800*	6 (OH-)
Phenol§	0.1 *N* HCl	210	6000	

**Ref. 5.* †*Ref. 7.* ‡*Ref. 13.* §*This series of papers.*

hydrogen bonding, field or inductive effects, and steric effects on the primary substituent are likely to affect the absorption. An illustration of the effect of intramolecular hydrogen bonding may be provided by the spectrum of *o*-nitrophenol, which on the basis of infrared measurements (16) is believed to exist in the hydrogen-bonded form. Steric effects on the primary substituent may be assumed to occur when both ortho substituents are large. In this way, *two* steric interactions between the two vicinal substituents may occur. First, one of the two substituents may remain in the plane of the benzene ring whereas the other is twisted away from this plane. This represents a common type of steric effect as indicated both by the data recorded in the present communication and from infrared data (cf. 17). Secondly, as steric interaction further increases, the coplanarity of *both* substituents with the plane of the benzene ring may be affected. An example of this may be provided by the spectrum of *o*-chloronitrobenzene in Table II. It may be supposed that there the chloro substituent is sufficiently dislodged from the plane of the benzene ring to prevent appreciable resonance interaction between the chlorine atom and the nitro group. At the same time, the nitro group also twists in order to reduce interaction between the two vicinal substituents, and consequently the absorption of *o*-chloronitrobenzene is not that of nitrobenzene but rather that of nitrobenzene sterically hindered.

It should also be noted that the above interactions in ortho isomers may not be entirely steric in origin, since short-range inductive or field effect interactions, for example between the chloro and nitro substitutents, may contribute to the observed effect. The latter type of interaction has previously been briefly discussed for fluoro substituents (18), and may be assumed to play a part in determining spectra. Further, in this section the buttressing effect may be mentioned since it may partly account for some of the anomalous values, for example the hypsochromic shift observed in *m*-chloronitrobenzene compared with nitrobenzene (cf. 19).

THE NATURE OF THE SHORT-RANGE INTERACTION

It was shown in the previous section that sometimes the series, monosubstituted parent compound, ortho- and meta-disubstituted compound, exhibits very similar B-band maximal wavelengths (cf. for example the spectral data of acetophenone and *o*- and *m*-chloroacetophenone in Table II). In others an effect of the second substituent on the benzene ring must first be taken into account before the wavelength values are comparable. This effect has been described as a "short-range" interaction, to distinguish it from interaction which is associated with electron mobility acting along systems of conjugated bonds (mesomeric interaction). This nomenclature is based on the observation that the interaction, in the absence of other factors (see above), appears to be similar in both ortho and meta positions, and, further, the similarity of the spectra apparently still exists even if the ortho isomer is most probably non-planar (cf. for example the spectra of the toluic acids in concentrated sulphuric acid as shown in Table II).

The second point concerning the nature of this interaction is that we consider it to be of minor importance compared with the major interactions (steric and mesomeric effects) determining electronic absorption spectra. This may be deduced from the magnitude of the wavelengths shifts caused by the interactions. For example, whereas the average wavelength displacements, because of the short-range interaction, for the two substituents described in Table II are -Me 5.5 mμ, and -OH 7 mμ, the corresponding wavelength shifts caused by mesomeric interaction (as judged for shifts obtained in the parasubstituted acetophenones) are -Me 12 mμ, and -OH 14 mμ (2, 3). Even if the short-range interaction is large, as for NH_2 and O^- substituents, when wavelength shifts of up to

25 mμ are obtained, the corresponding wavelength shifts because of mesomeric interaction in the acetophenone series are 76 mμ (2) and 79 mμ (7) respectively, that is, very much larger. Further, since steric interaction can completely inhibit mesomeric interaction, both may be considered to be of similar importance in electronic spectra. Consequently, we conclude that if in substituted benzene derivatives mesomeric interaction is possible, this will normally determine predominantly the B-band of electronic absorption spectra, while the other, short-range interaction is only of secondary importance. We may also note in passing that this short-range interaction probably corresponds to the interaction deduced theoretically by Förster (6). Both these considerations point against a residual mesomeric interaction which still operates in the ortho isomer. This follows because the interaction is discernible in both ortho and meta positions to a similar extent, and is not generally more enhanced in the ortho position, as would be expected for a residual mesomeric interaction. Further, precisely such a residual mesomeric interaction may partly account for the occasional bathochromic wavelength displacement observed for the ortho isomer (see, for example, the spectra of chlorobenzaldehydes in Table II), and under these circumstances the expected bathochromic displacement relative to the meta isomer *is* obtained.

Next, it follows from theoretical considerations (cf. 20) that when both short-range and mesomeric interactions operate and when both are appreciable, the total effect will almost certainly not be simply additive but will follow a more complex pattern. This will be of importance for many paradisubstituted and, incidentally, monosubstituted benzene derivatives and may account for some of the anomalous mesomeric interactions. For example, Doub and Vandenbelt (5) found that nitro compounds frequently do not fit the normal displacement patterns; and this anomaly may be related to the relatively large short-range interaction for the nitro group (15, 21). A similar lack of additivity also prevails if more than one substituent contributes to the short-range interaction exerted on the benzene ring (cf. section on trisubstituted benzene derivatives). This again is more pronounced if the short-range interaction is large, as for example in *m*-diaminobenzene, which absorbs maximally at 240 mμ, the second amino substituent in this way causing a wavelength shift of only about 5 mμ (5).

Further, it may be noted that the order of magnitude for the short-range interaction may be related qualitatively both to the order observed for frequency displacements in some vibrational spectra and to the order of acidity constants for some aromatic acids. For example, the asymmetric stretching vibrations of nitrobenzenes are shifted to lower frequency (i.e. to longer wavelength) for meta substituents in the order $-NH_2 > -H > -NO_2$ (17), and this is qualitatively the same order as for the acidity-constant decreases in metasubstituted benzoic acids (22) and for the present short-range interactions. Generally—and this is by no means intended to rule out exceptions—all these effects will presumably be determined largely by the over-all electronegativity and hence these data may be expected to correlate also with the inductive effect. This is in fact indicated since the order for the halogens in their short-range interactions sometimes suggests the order of the inductive effects. For example, Ungnade (23) reports an order of $-F > -Cl > -Br > -I$ for the negative wave-length displacements relative to nitrobenzene. However, the inductive effect does not fully explain many of the wavelength displacements caused by the short-range interaction and hence it is preferable to consider the over-all electronegativity independently for each set of examples (15).

It also follows from the above considerations that it will normally be difficult to detect short-range interactions in the electronic absorption spectra of paradisubstituted benzene

derivatives. Exceptions may occur in compounds where the mesomeric interaction is relatively small compared with the short-range interaction. Examples of this may be provided by the various *p*-alkylsubstituted compounds which exhibit wavelength shifts in the order -*tert*-butyl > -methyl, i.e. in the order of their over-all inductive effects (cf. 24, 25).

THE B-BANDS OF TRISUBSTITUTED BENZENE DERIVATIVES

From a consideration of the previous sections it might be anticipated that the B-band spectra of trisubstituted benzene derivatives will normally be determined by the interaction of the two substituents, which when linked to the phenyl ring give rise to maximum resonance interaction and thus cause absorption at longest wavelength; the remaining substituent would be expected to exert only the short-range interaction. This expectation is supported by the observed spectra (see Table III). The data are largely those determined by Doub and Vandenbelt (13) who have already shown that the B-bands of trisubstituted benzene derivatives often closely resemble the most displaced B-band of one of the disubstituted parent compounds.

We can now relate this observation with our previous hypotheses by again postulating that one of the three substituents because of steric interactions no longer, or only partly, contributes to the observed B-band. Without introducing any additional hypotheses the data in this way correlate well with expectation. More precisely, the effects of the third substituent on the wavelength of the B-band can be classified into three types. The substituent may be almost completely dislodged, when the spectrum of the trisubstituted benzene derivative will closely resemble that of the disubstituted parent compound (see Table III, Section A). The latter is usually the para compound, but if the absorption of one of the meta or ortho isomers occurs at longer wavelength (i.e. is caused by an energetically more favorable transition) than that of the para compound, the absorption of the trisubstituted benzene derivative may resemble that of the meta or ortho isomer; the spectrum of the trisubstituted benzene derivative may also resemble that of the monosubstituted benzene derivative, if interaction between any two substituents is small. This is illustrated for a number of 2,5-disubstituted benzoic acids for which benzoic acid may be taken as the reference compound (see Table III, Section A). Sometimes also two B-bands occur for trisubstituted benzene derivatives, one corresponding to the ortho isomer and the other to the para isomer (15, cf. also 26).

Examples where some interaction with the third substituent occurs are illustrated in Section B of Table III which lists compounds where the ortho substituent makes some resonance contribution and in this way causes a bathochromic displacement of more than 5 mμ. In accordance with expectation this displacement only occurs if the vicinal ortho substituents are small, or if the interaction is essentially π–p bond interaction, which has been shown to be less direction-dependent than other interactions (3). This additional resonance interaction incidentally is assumed to include intramolecular hydrogen bonding and it should also be noted that the interaction may contribute to some of the lesser ortho effects shown in Section A of Table III. This follows because the anticipated bathochromic displacement may be cancelled out by steric effects as described in the succeeding paragraph.

Section C of Table III lists examples where the ortho substituent interferes appreciably with the resonance interaction of the reference compound and thereby gives rise to a hypsochromic wavelength displacement. This type of displacement has already been ascribed to steric effects on the primary substituent (see section on "Steric effects in acid

TABLE III

B-BANDS OF TRISUBSTITUTED BENZENE DERIVATIVES AND SUITABLE REFERENCE COMPOUNDS

Solvent	Trisubstituted derivative* Compound	$\lambda_{max.}$ mμ	ϵ_{max}	Reference compound Compound	$\lambda_{max.}$ mμ	ϵ_{max}
	A. B-bands of trisubstituted benzene and reference compound are within 5 mμ					
pH 3	2-Hydroxy-4-toluic acid	242	9600	*p*-Toluic acid†	241.5	14400
pH 7	3,4-Dihydroxybenzoic acid	251	7800	*p*-Hydroxybenzoic acid‡	251	12500
pH 11	2,4-Dimethoxybenzoic acid	246	8500	*p*-Anisic acid†	247	14000
pH 11	3-Amino-4-hydroxybenzoic acid	280	9200	*p*-Hydroxybenzoic acid†	280	16300
0.1 *N* HCl	3,4-Dihydroxyacetophenone	274	9900	*p*-Hydroxyacetophenone†	275	14300
pH 11	2,4-Dihydroxybenzaldehyde	331	20300	*p*-Hydroxybenzaldehyde†	330	27900
H_2O	2,5-Dimethoxynitrobenzene	273	3300	*m*-Nitroanisole§	273.5	6000
H_2O	2-Methoxy-5-chloronitrobenzene	265	3900	*m*-Chloronitrobenzene§	264	7100
pH 3	3,4-Dichlorobenzoic acid	242	13500	*p*-Chlorobenzoic acid†	241	16300
pH 11	3,4-Dichlorobenzoic acid	237	11300	*p*-Chlorobenzoic acid†	235	13600
pH 7	2-Hydroxy-4-toluic acid	238	8500	*p*-Toluic acid‡	236	14000
0.1 *N* HCl	2,4-Dihydroxybenzoic acid	256	13600	*p*-Hydroxybenzoic acid†	255	13900
pH 7	2,4-Dihydroxybenzoic acid	248	10800	*p*-Hydroxybenzoic acid‡	251	12500
pH 3	3,4-Dihydroxybenzoic acid	260	9300	*p*-Hydroxybenzoic acid†	255	13900
pH 11	3,4-Dihydroxybenzoic acid	276	8000	*p*-Hydroxybenzoic acid†	280	16300
pH 3	3-Methoxy-4-hydroxybenzoic acid	260	11100	*p*-Hydroxybenzoic acid†	255	13900
pH 7	3-Methoxy-4-hydroxybenzoic acid	251	9900	*p*-Hydroxybenzoic acid‡	251	12500
0.1 *N* NaOH	3-Methoxy-4-hydroxybenzoic acid	*280*	*13000*	*p*-Hydroxybenzoic acid†	280	16300
pH 3	2-Hydroxy-4-anisic acid	254	12400	*p*-Anisic acid†	256.5	15900
pH 7	2-Hydroxy-4-anisic acid	250	12000	*p*-Anisic acid‡	249	14000
pH 3	2,4-Dimethoxybenzoic acid	257	13100	*p*-Anisic acid†	256.5	15900
pH 7	3-Amino-4-hydroxybenzoic acid	253	6900	*p*-Hydroxybenzoic acid‡	251	12500
pH 3.6	2-Methyl-4-aminobenzoic acid	223	9600	*p*-Aminobenzoic acid†	219.5	9900
pH 11	2-Methyl-4-aminobenzoic acid	266	12200	*p*-Aminobenzoic acid†	265	14900
pH 11	2,4-Diaminobenzoic acid	266	10000	*p*-Aminobenzoic acid†	265	14900
H_2O	2,4-Dichloroacetophenone	252	8900	*p*-Chloroacetophenone*	254.5	16300
H_2O	3,4-Dichloroacetophenone	254	14600	*p*-Chloroacetophenone*	254.5	16300
pH 3	2,4-Dihydroxyacetophenone	275	13900	*p*-Hydroxyacetophenone†	275	14300
pH 11	2,4-Dihydroxyacetophenone	328	25600	*p*-Hydroxyacetophenone†	324.5	23100
pH 6	2-Hydroxy-4-aminoacetophenone	245	5700	*p*-Aminoacetophenone†	240	13000
H_2O	2,4-Dichlorobenzaldehyde	263	13700	*p*-Chlorobenzaldehyde*	259.5	17400
pH 3	2,4-Dihydroxybenzaldehyde	278	15700	*p*-Hydroxybenzaldehyde†	283.5	16000
H_2O	3,4-Dichloronitrobenzene	276	9200	*p*-Chloronitrobenzene†	280	10300
0.1 *N* HCl	2-Chloro-4-nitrophenol	317	8500	*p*-Nitrophenol†	317.5	10000
0.1 *N* NaOH	2-Chloro-4-nitrophenol	400	17400	*p*-Nitrophenol†	402.5	19200
pH 5	2-Amino-4-nitrophenol	315	5100	*p*-Nitrophenol†	317.5	10000
0.1 *N* HCl	2-Hydroxy-5-chlorobenzoic acid	233	7700	Benzoic acid‡	229.5	11500
pH 7	2-Hydroxy-5-chlorobenzoic acid	230	7900	Benzoic acid‡	226	9500
0.1 *N* HCl	2-Hydroxy-5-bromobenzoic acid	233	8400	Benzoic acid‡	229.5	11500
pH 7	2-Hydroxy-5-bromobenzoic acid	*232*	*8400*	Salicylic acid§	237	9000
0.1 *N* HCl	2,5-Dihydroxybenzoic acid	238	9300	*m*-Hydroxybenzoic acid§	236.5	7500
pH 7	2,5-Dihydroxybenzoic acid	*235*	*8300*	*m*-Hydroxybenzoic acid§	*232*	*6400*
pH 3	2-Methoxy-5-bromobenzoic acid	*234*	*9000*	Benzoic acid‡	229.5	11500
pH 3	2-Amino-5-chlorobenzoic acid	218	22000	*m*-Aminobenzoic acid§	218.5	14000
H_2O	2,5-Dichloroacetophenone	240	6200	Acetophenone‡	244	12000
0.1 *N* HCl	2,5-Dihydroxyacetophenone	256	9400	*o*-Hydroxyacetophenone§	252.5	10900
pH 3	2-Hydroxy-5-chlorobenzaldehyde	255	8900	*o*-Hydroxybenzaldehyde§	256	12600
0.1 *N* NaOH	2-Hydroxy-5-chlorobenzaldehyde	*260*	*7600*	*o*-Hydroxybenzaldehyde§	264.5	7500
H_2O	2-Methyl-5-chloronitrobenzene	262	4800	*m*-Chloronitrobenzene§	264	7100
pH 11	4-Methoxy-2-nitroaniline	285	5200	*o*-Nitroaniline	282.5	5400
	B. Orthosubstituent causes shift of more than 5 mμ towards longer wavelength					
pH 3.1	2-Hydroxy-4-aminobenzoic acid	231	8300¶	*p*-Aminobenzoic acid†	219.5	9900
pH 4.4	2,4-Diaminobenzoic acid	228	16400	*p*-Aminobenzoic acid†	219.5	9900
pH 3	2-Chloro-4-aminobenzoic acid	*225*	*9500*	*p*-Aminobenzoic acid†	219.5	9900
pH 4	2-Amino-4-chlorobenzoic acid	249	8900	*p*-Chlorobenzoic acid†	241	16300
pH 7	2-Amino-4-chlorobenzoic acid	247	8500	*p*-Chlorobenzoic acid‡	234	15000
pH 11	2,4-Dihydroxybenzoic acid	298	13000	*p*-Hydroxybenzoic acid†	280	16300
pH 11	3,4-Dihydroxyacetophenone	342	16300	*p*-Hydroxyacetophenone†	324.5	23100
0.1 *N* NaOH	2-Hydroxy-4-aminoacetophenone	348	10400	*p*-Aminoacetophenone†	311.5	17100
pH 11	2-Amino-4-nitrotoluene	293	5800	*p*-Nitrotoluene†	285	9250
pH 11	2-Amino-4-nitrophenol	446	13400	*p*-Nitrophenol†	402.5	19200
pH 7	2-Methoxy-4-nitroaniline	400	12300	*p*-Nitroaniline†	381	13500
pH 11	2-Amino-4-nitroaniline	402	9000	*p*-Nitroaniline†	381	13500
	C. Orthosubstituent causes shift of more than 5 mμ towards shorter wavelength					
pH 3	2,4-Dichlorobenzoic acid	232	7400	*p*-Chlorobenzoic acid†	241	16300
pH 11	2,4-Dichlorobenzoic acid	229	7400	*p*-Chlorobenzoic acid†	235	13600
pH 7	2-Hydroxy-4-aminobenzoic acid	265	13200	*p*-Aminobenzoic acid‡	288	19000
pH 7	2-Chloro-4-aminobenzoic acid	256	9000	*p*-Aminobenzoic acid‡	288	19000
H_2O	2,5-Dichloronitrobenzene	258	3300	*m*-Chloronitrobenzene§	264	7100

**Ref. 13.*
†Ref. 7.
‡This series of papers.
§Ref. 5.
¶Doub and Vandenbelt (13) refer to this band as the secondary primary band while designating the band at 275 mμ as the first primary band (B-band). Further in p-aminobenzoic acid the 270 mμ band is referred to (4) as the secondary band (C-band) and the band at 226.5 mμ as the first primary band. Our interpretation is to regard both the bands at 226.5 and 231 mμ as B-bands (first primary bands) and the bands at 270 and 275 mμ as C-bands (secondary bands). A similar reassignment has also been assumed for a number of other compounds in this table.

and basic media"). The explanation now receives support since the shift is usually associated with decreased absorption intensity, and most frequently occurs if the third substituent is large or if the primary substituent is sensitive to steric interaction as for example in neutral solution (see Section C of Table III). Again steric effects of this type are also evident to a lesser extent in the other sections of Table III, particularly noticeable being the frequent loss of absorption intensity in the trisubstituted compound.

EXPERIMENTAL

All spectra were determined in duplicate on a Unicam SP. 500 spectrophotometer with 1 cm. quartz cells. Where applicable, the data obtained compared well with previous data reported in the literature.

Commercial samples, purified by crystallization or distillation, were used. Sodium hydroxide (1 *N*) was made up immediately before use from Fisher Certified pellets ($Na_2CO_3 < 0.5\%$), or when necessary from 5 *N* sodium hydroxide, volumetric solution, carbonate-free.

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NOTES

2-BENZHYDRYLIMINO-4-THIAZOLIDONES AND RELATED COMPOUNDS

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The synthesis of a series of 1-benzhydryl-2-alkyl-2-thiopseudoureas has recently been reported from this laboratory (1). These compounds exhibited a central stimulating action when administered to experimental animals. In the present investigation, certain cyclic thiopseudoureas with a structural relationship to the above compounds were prepared and screened for their pharmacological activity. The preparation of the 1-benzhydrylthioureas used in the present study was described in the previous paper (1).

The reaction of an unsymmetrically substituted thiourea with an α-haloester may produce one of two possible isomeric 4-thiazolidones depending on the manner in which the cyclization occurs (2). Thus 1-benzhydrylthiourea and ethyl α-bromoacetate yielded either 2-benzhydrylimino-4-thiazolidone or 3-benzhydryl-2-imino-4-thiazolidone. A proof of structure was carried out by the method of Davis and Dains (3). Condensation with benzaldehyde in the presence of piperidine gave 2-benzhydrylimino-5-benzal-4-thiazolidone which was then hydrolyzed by hydrochloric acid to yield 5-benzal-2,4-thiazolidinedione, a known compound. Other 1-benzhydrylthioureas and other α-haloesters gave 2-benzhydrylimino-4-thiazolidones substituted in the 3 and the 5 positions. They are listed in Table I.

2-Benzhydrylaminothiazole has been prepared by Kaye (4) from 1-benzhydrylthiourea and dimethyl chloroacetal. In a like manner 1-benzhydrylthiourea and α-chloroacetone gave 2-benzhydrylamino-4-methylthiazole. The reaction of 1-benzhydrylthiourea with β-iodopropionic acid gave 2-benzhydrylimino-4-keto-1,3-thiazane. The preparation of some 2-alkylimino-4-keto-1,3-thiazanes by a similar procedure has been reported (5). Bose and Nandi (6) have shown that the reaction between a 1-alkylthiosemicarbazide and ethyl α-chloroacetate yields a 2-alkylimino-5-keto-1,3,4-thiadiazane and not a 2-alkylamino-3-amino-4-thiazolidone. In the present investigation, 1-benzhydrylthiosemicarbazide and ethyl α-chloroacetate gave 2-benzhydrylimino-5-keto-1,3,4-thiadiazane.

Some of the cyclic thiopseudoureas were found to be central-nervous-system depressants. This is in contrast to the stimulant properties shown by the acyclic benzhydrylthiopseudoureas.

EXPERIMENTAL*

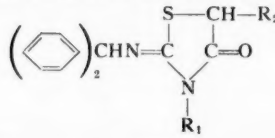
2-Benzhydrylimino-4-thiazolidone.—A solution of 1-benzhydrylthiourea (2.42 g., 0.01 mole) and ethyl α-bromoacetate (2.5 g., 0.015 mole) in 75 ml. of ethanol was allowed to stand for 16 hours at room temperature. Ether was then added to ensure complete precipitation of the product, which was filtered off and dried to yield 2.17 g., m.p. 252°–253° C. One recrystallization from 2-propanol did not change the melting point (see Table I).

2-Benzhydrylimino-5-methyl-4-thiazolidone.—1-Benzhydrylthiourea (4.8 g., 0.02 mole) and ethyl α-bromopropionate were dissolved in 50 ml. of glacial acetic acid and the solution refluxed for 16 hours. On cooling and addition of water, the product precipitated,

**All melting points are uncorrected.*

TABLE I

2-BENZHYDRYLIMINO-4-THIAZOLIDONES



R_1	R_2	Yield, %	M.p., °C.	Formula	Carbon		Hydrogen		Nitrogen		Sulphur	
					Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
H	H	77	252–253	$C_{16}H_{14}N_2SO$	68.15	68.57	4.98	5.34	9.92	9.63	11.33	11.22
H	CH_3	81	245–246	$C_{17}H_{16}N_2SO$					9.45	9.44	10.82	10.71
H[a]	CH_2CH_3	81	215–216	$C_{18}H_{18}N_2SO$	69.65	69.81	5.85	5.74	9.03	8.93	10.33	10.23
H	$CH_2CH_2CH_2CH_3$	72	196–197	$C_{20}H_{22}N_2SO$					8.27	8.08	9.46	9.30
CH_3	H	54	104–105	$C_{17}H_{16}N_2SO$	68.91	69.07	5.42	5.44	9.45	9.25	10.82	10.99
CH_2CH_2OH[b]	H	51	174–175	$C_{18}H_{19}N_2SO_2Cl$[c]	59.60	59.33	5.27	5.26	7.72	7.66	8.83	8.81

[a] *Hydrobromide melts at 181°–183° C. Calculated for* $C_{18}H_{19}N_2OBrS$: N, *7.16;* Br, *20.44. Found:* N, *7.33;* Br, *20.44.*
[b] *This compound was isolated as its hydrochloride.*
[c] *Chlorine: Calc., 9.77; found, 9.84.*

4.8 g., m.p. 195°–208° C. Two recrystallizations from ethanol raised the melting point to 245°–246° C. (see Table I).

2-Benzhydrylimino-3-hydroxyethyl-4-thiazolidone hydrochloride. — 1-Benzhydryl-3-hydroxyethylthiourea (5.7 g., 0.02 mole) and α-chloroacetic acid (1.9 g., 0.02 mole) in 25 ml. of 2-propanol containing sodium acetate (1.6 g., 0.02 mole) were refluxed for 1 hour. The sodium chloride was then removed and an excess of ethereal hydrogen chloride was added to the filtrate causing the product hydrochloride to separate, 3.7 g., m.p. 168°–169° C. Two recrystallizations from a methanol–ether mixture raised the melting point to 174°–175° C. (see Table I).

2-Benzhydrylimino-5-benzal-4-thiazolidone.—2-Benzhydrylimino-4-thiazolidone (2.6 g., 0.009 mole) and benzaldehyde (0.95 g., 0.009 mole) were dissolved in 10 ml. of absolute ethanol containing a few drops of piperidine. The reaction mixture was refluxed for 2 hours. On cooling, 2.6 g. of product precipitated, m.p. 252°–257° C. Two recrystallizations from a large amount of ethanol raised the melting point to 265°–268° C. Calc. for $C_{23}H_{18}N_2SO$: N, 7.54; S, 8.65. Found: N, 7.82; S, 8.71.

5-Benzal-2,4-thiazolidinedione.—2-Benzhydrylimino-5-benzal-4-thiazolidone (0.3 g.) was dissolved in a solution of 80 ml. ethanol and 40 ml. concentrated hydrochloric acid. The reaction mixture was refluxed for 24 hours. On cooling and removal of the ethanol *in vacuo*, the product precipitated, 0.08 g., m.p. 246°–247° C. (lit. m.p. 243° C.) (3). Calc. for $C_{10}H_7NSO_2$: S, 15.62. Found: S, 15.35.

2-Benzhydrylamino-4-methylthiazole hydrochloride.—1-Benzhydrylthiourea (4.8 g., 0.02 mole) and α-chloroacetone (2.03 g., 0.022 mole) were dissolved in 150 ml. of 1:1 ether–acetone solution. The reaction mixture was allowed to stand at room temperature for 16 hours during which time the product hydrochloride precipitated, 3.3 g., m.p. 188°–189° C. One recrystallization from ethanol did not change the melting point. Calc. for $C_{17}H_{17}N_2SCl$: C, 64.39; H, 5.36; N, 8.84; S, 10.03. Found: C, 64.48; H, 5.23; N, 9.01; S, 10.03.

2-Benzhydrylimino-4-keto-1,3-thiazane hydroiodide.—1-Benzhydrylthiourea (4.8 g., 0.02 mole) and β-iodopropionic acid (4.0 g., 0.02 mole) were dissolved in 50 ml. of absolute ethanol and the solution refluxed for 4 hours. The ethanol was then removed *in vacuo* and 25 ml. of acetic anhydride added. The reaction mixture was again heated for 4 hours on a steam bath. On cooling and addition of ether, 6.1 g. of product separated out, m.p. 191°–193° C. dec. One recrystallization from acetonitrile did not change the melting point. Calc. for $C_{17}H_{17}N_2SIO$: N, 6.62; S, 7.55; I, 29.95. Found: N, 6.98; S, 7.91; I, 30.00.

2-Benzhydrylimino-5-keto-1,3,4-thiadiazane.—1-Benzhydrylthiosemicarbazide (8.9 g., 0.032 mole), α-chloroacetic acid (3.0 g., 0.032 mole), and sodium acetate (2.6 g., 0.032 mole) were added to 75 ml. of 2-propanol and refluxed for 4 hours. Water was then added causing the product to separate out as an oil, which eventually solidified to yield 7.6 g., m.p. 114°–124° C. Two recrystallizations from ethanol gave an analytically pure material, m.p. 141°–142° C. Calc. for $C_{16}H_{15}N_3SO$: C, 64.62; H, 5.09; N, 14.13; S, 10.77. Found: C, 64.80; H, 4.94; N, 14.10; S, 10.68.

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Contents

R. Tremblay, A. F. Sirianni, and I. E. Puddington—The molecular weight of polyethylene and of other high-molecular-weight organic compounds - - 725

J. C. Roy, P. J. Berry, and L. P. Roy—Reactor neutron-capture cross section of 18-minute Rb^{88} - - - - - - - - - - - - - - - - - - 731

Paul E. Gagnon, Jean L. Boivin, Paul A. Boivin, and John H. Dickson— Alkylguanidine nitrates and alkylnitroguanidines - - - - - - - - - - 737

D. K. Thomas and O. Maass—Electrolytic conductance in hydrogen peroxide–water mixtures. Part II. Some monobasic and dibasic acids - - - - - 744

Marshall Kulka—Seven- and eight-membered rings containing carbon and two sulphur atoms - - - - - - - - - - - - - - - - - - - 750

G. A. Adams—Structure of an arabogalactan from white spruce (*Picea glauca* (Moench) Voss) - - - - - - - - - - - - - - - - - - 755

F. A. L. Anet and P. M. G. Bavin—Studies in the Wagner–Meerwein rearrangement. Part III - - - - - - - - - - - - - - - - - - - 763

Ragini Anet and Léo Marion—Some structural features of delcosine - - - 766

John C. Grivas and Alfred Taurins—Reaction of trichloroacetonitrile with primary and secondary amines. Part I. Preparation of some trichloroacetamidines - 771

M.-E. Kreling and A. F. McKay—Some new sulphonamides and derivatives of bicyclic guanidines - - - - - - - - - - - - - - - - - - 775

S. N. Flengas and T. R. Ingraham—Voltaic cells in fused salts. Part III. The system silver – silver chloride, cadmium – cadmium chloride - - - - - 780

T. C. Waddington and W. G. Schneider—The effect of the ambient gases on the surface photocurrent in anthracene - - - - - - - - - - - 789

L. W. Reeves and W. G. Schneider—Nuclear magnetic resonance measurements of proton transfers in acetylacetone in diethylamine and triethylamine - 793

Eugene Lieber, C. N. R. Rao, C. N. Pillai, J. Ramachandran, and Ralph D. Hites—The infrared spectra of 4-substituted-thiosemicarbazides and diazotization products - - - - - - - - - - - - - - - - 801

A. S. Perlin—Radiochemical evidence for heterogeneity in wheat starch - - 810

P. Brassard and P. L'Écuyer—L'arylation des quinones par les sels diazonium. III. Sur la synthèse des aryl-chloro-*p*-benzoquinones - - - - - - - 814

R. A. McIvor, C. E. Hubley, G. A. Grant, and A. A. Grey—The infrared spectra of organo-phosphorus compounds. II. The 1–2.6 μ region - - - - - - - 820

S. S. Berman and W. A. E. McBryde—Separations of the platinum metals by ion exchange - - - - - - - - - - - - - - - - - - - 835

S. S. Berman and W. A. E. McBryde—The separation of rhodium and iridium by ion exchange - - - - - - - - - - - - - - - - - - 845

R. A. Heacock, C. Nerenberg, and A. N. Payza—The chemistry of the "aminochromes". Part I. The preparation and paper chromatography of pure adrenochrome - - - - - - - - - - - - - - - - - - 853

J. A. Manson and L. H. Cragg—A study of graft copolymers. I. Preparation and viscosity behavior - - - - - - - - - - - - - - - - - 858

W. F. Forbes, Audrey S. Ralph, and (in part) Rosemarie Gosine— Light-absorption studies. Part X. Ultraviolet spectra in acid and basic media—some further observations on the ortho effect - - - - - - - - - - - 869

Notes:

Stanley O. Winthrop and Gregory Gavin—2-Benzhydrylimino-4-thiazolidones and related compounds - - - - - - - - - - - - - - 879

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